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TRANSACTIONS

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Vol. 122

INSTITUTE OF METALS DIVISION 1936

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD
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This volume is the tenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Chicago Meeting, Oct. 1-3, 1935 and the New York Meeting, Feb. 17-20, 1936. The complete list of publications and proceedings, including the present volume, is as follows:

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1912-1916 *Transactions* of the American Institute of Metals, Vols. 6-10.

1917-1918 *Journal* of the American Institute of Metals, Vols. 11-12.

1919-1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927-1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. TRANSACTIONS.

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FOREWORD

This volume is the tenth of the series of TRANSACTIONS presenting separately the publications of the Institute of Metals Division. At the suggestion of the Papers and Publications Committee, and with the approval of the Executive Committee, we have returned to the publication policy in force prior to the "depression"; that is, the annual volumes will contain papers published at the annual February meeting and those of the *preceding* divisional meeting. This procedure has the advantage of permitting earlier publication of the TRANSACTIONS volume but, because many of the papers of the 1935 divisional meeting were included in the 1935 volume, the present one is relatively small.

The papers in this volume show considerable interest in the mechanism of age-hardening and the constitution of alloy systems and the related subject of diffusion in metals. The Institute of Metals Division lecture, by Robert F. Mehl, constitutes a valuable addition and is a masterful presentation of the subject of diffusion in solid metals.

It is a pleasure at this time to be able to call attention to the reciprocal membership privileges between the A.I.M.E. and the British Institute of Metals, negotiations for which were started last year by Dr. Paul D. Merica and Past Chairman W. M. Peirce. According to this arrangement, any member of one society that has not passed his thirty-third birthday may join the other society on especially favorable terms.

The thanks of the Chairman, the Executive Committee, and members of the Institute of Metals Division are tendered to members of the Papers and Publications Committee, under the able Chairmanship of Dr. R. F. Mehl, and to the authors of the papers composing this splendid volume.

E. H. DIX, JR., *Chairman*,
Institute of Metals Division.

NEW KENSINGTON, PA.
November 9, 1936.

THE INSTITUTE OF METALS LECTURE

AN annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.
- 1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
- 1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
- 1935 Gases in Metals. By C. A. Edwards.
- 1936 Diffusion in Solid Metals. By Robert F. Mehl.

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¹ Until February, 1937. ² Until February, 1938. ³ Until February, 1939.

ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February.

There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmānstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. *TRANSACTIONS* (1931) **93**, 78–110.
- 1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. *TRANSACTIONS* (1934) **111**, 264–292.
- 1936 Cyril S. Smith and W. Earl Lindlief: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. *TRANSACTIONS* (1933) **104**, 69–105.



ROBERT F. MEHL
Institute of Metals Division Lecturer, 1936

Diffusion in Solid Metals

BY ROBERT F. MEHL,* MEMBER A.I.M.E.

(Institute of Metals Division Lecture†)

IN examining the progress of metallurgical science, the critic must remember that most of our present knowledge of metals and alloys has been accumulated through the needs of industry and commerce rather than through the desire and efforts of a large body of scientists interested primarily in developing a science of metals. The progress of metallurgy, scientifically speaking, has been irregular, and little given to the exhaustive exploitation of important scientific fields.

The experienced engineer now recognizes the need for the development of the basic science upon which his engineering rests. In addition to the increase in knowledge which results from the normal requirements of industry, a development of the basic science of the behavior of metals and alloys is as desirable in metallurgy as in any other branch of science and engineering. The continued growth of the science of metals—as of every other science—requires studious attention to the principles that underlie the behavior of matter, with the result that knowledge in the several fields of interest should continue to increase.

Among the various subjects recognized as important in physical metallurgy few have a wider significance than that of diffusion in solid metals. The phenomena of diffusion are intimately related to many basic problems of the metallic state, but in addition to this, the process of diffusion is of first importance practically. The formation of alloys by the annealing of mixed powders, first practiced by Faraday and Stodart⁸¹† in 1820 and in more recent years investigated by Masing^{187,189} and others, has led to the development of special alloys like Carboloy, Vascoloy-Ramet, Genelite, Elcon⁶⁸, and has recently been applied to the production of noble-metal alloys for electrical contacts¹⁸².

The early work on carburization^{8,97} has led to similar work on the improvement of metal surfaces by the diffusion inwards of various metals and nonmetals, leading to the development—apart from carburizing

* Professor of Metallurgy, and Director, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

† Presented at the New York meeting, February, 1936. Fifteenth annual lecture. As printed here the lecture is an extended form of that presented. Manuscript received at the office of the Institute May 4, 1936.

‡ References are at the end of the paper.

itself—of the processes of calorizing, sherardizing, chromizing, nitriding, and to processes for the development of bimetal strip and veneer metals²¹⁸. The highly interesting paper by L. C. Grimshaw¹⁰¹ describes the modern aspects of the latter process. But the process of diffusion has a wider importance than this: the homogenization of segregated alloys, the rates of transformation and of precipitation, and therefore the rates of hardening of steel and of age-hardening of alloys of the duralumin type, depend to a greater or lesser degree upon the rates of diffusion. Since diffusion evidently involves atomic movements, the rates of diffusion must be determined by the possible energy states of the atom and are therefore intimately related to the physics of the solid state.

Judging from the slow rate of diffusion in inorganic salts and from the lack of diffusion in rocks during geologic eras, it was once thought that diffusion in the solid state must be infinitesimally slow compared to that obtaining in liquids. Although Spring²⁵⁵⁻²⁵⁷ had shown in 1884 that metals may interpenetrate by diffusion, and indeed it had been shown earlier that C will rapidly penetrate into γ Fe, the high value of the diffusion coefficient of Au in Pb as measured by Roberts-Austen²²⁰⁻²²² in 1896 came as a surprise. In the following years research on diffusion was rather sporadic, but the increasing interest in the electrical conductivity of salt crystals led to research which carried many implications for metal systems and shortly resulted in a series of important papers on diffusion in metals. This, together with the rapid advance of physical metallurgy in all of its parts and with an increasing realization of the practical importance of the subject of diffusion, has produced a large body of information, which, though not yet sufficiently complete to be considered well developed, is interesting and valuable enough to warrant reviewing and criticism.

METHODS

The modern quantitative treatment of diffusion in solid metals is on the basis of Fick's law⁸², derived by analogy from Fourier's law of heat flow, in which the diffusing solute is treated analogously to heat. Stefan²⁵⁸ gave solutions to Fick's equation and applied them to Graham's⁹⁹ measurements on diffusion in liquid solution, showing this diffusion to be consistent with Fick's law. Stefan prepared tables facilitating the calculation of the diffusion coefficient for the experimental conditions under which Graham's data were obtained, and these tables were later amplified by Kawalki¹⁶⁷ and by Jost¹⁵⁴. The mathematical treatment of diffusion has been somewhat amplified by later workers as indicated below.

Fick's law is

$$dm = D \cdot A \cdot \frac{dc}{dx} \cdot dt \quad [1]$$

where dm is the amount of solute in grams diffusing in time dt through (and in the direction of) a concentration gradient $\frac{dc}{dx}$ across area A expressed in square centimeters; D is thus a proportionality factor, designated as the diffusion coefficient, *representing the amount of substance in grams diffusing in one second across an area of 1 sq. cm. through a unit concentration gradient*. It has the dimensions length²/time, as may be seen from inspection of equation 1, variously given in cm.²/day or cm.²/sec.

From equation 1 we may derive the differential equation

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad [2]$$

in which D is assumed independent of concentration, an assumption not valid in either liquid or solid solutions. Equation 2 may be solved for various boundary conditions imposed by the experimental procedure. As an illustration, we may take the original method of Stefan but use the tables of Kawalki, in which diffusion takes place from a solution of thickness $2x$ into pure solvent of thickness $6x$ (total $8x$); under these conditions, after a period of time the solute will have diffused across the interface and the concentration in the original $2x$ layer at every point will have decreased from its original value. Kawalki's tables give the values for

the quantity $\frac{x}{2\sqrt{Dt}}$ (symbols as above) for the concentration found in each x layer by analysis; with the proper value of $\frac{x}{2\sqrt{Dt}}$ determined,

D may be calculated since x and t are known. Disagreement in the values of D for the different layers signified a variation of D with concentration.

Van Orstrand and Dewey²¹⁰ solved equation 2 for the diffusion from a saturated solution containing undissolved solute (the concentration of which thus remains unchanged throughout the experiment) into pure solvent, obtaining the equation

$$c = c_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\omega^2} d\omega \right] \quad [3]$$

where c is the concentration of solute at any point along the direction of diffusion removed from the interface by the distance x , c_0 the saturation concentration, and ω merely an integration variable. The quantity to the right of the minus sign is the Gauss error function, ϕ , described as the probability integral in mathematical tables, values for which may be found in tables. We may then rewrite equation 3:

$$c = c_0 \left[1 - \phi \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad [4]$$

Thus a chemical analysis of composition at a series of points will give values of c , which with c_0 can be used to evaluate the error function ϕ ; tables will then give the value of the quantity $\frac{x}{2\sqrt{Dt}}$, and with x and t known, D can be calculated. Fig. 1 shows a plot of concentration against $\frac{x}{2\sqrt{Dt}}$; the curve thus represents a diffusion penetration curve for

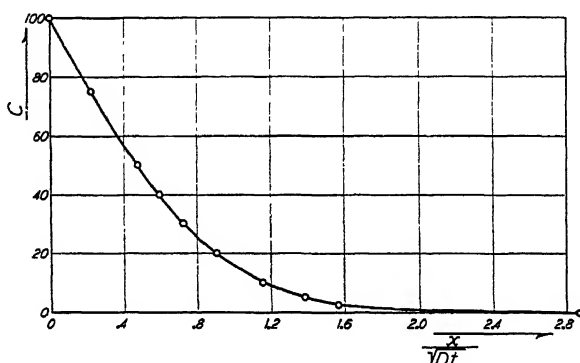


FIG. 1.—PLOT OF FUNCTION IN EQUATIONS 3 AND 4, REPRESENTING DIFFUSION PENETRATION CURVE¹⁸⁴.

a given value of D and t , and departures from this type of curve will represent variations of D with c (often designated in the literature as departures from Fick's law), or phase changes accompanying diffusion (Fig. 7).

Diffusion across an interface from a column of solution of infinite length, in reality in a system in which the concentration at the further end of the solution column remains unchanged, and at the further end of the solvent column remains zero, may be analyzed by the equation

$$c = \frac{c_0}{2} \left[1 - \phi \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad [5]$$

None of these equations provides for variation in D with concentration, though progressively changing values of D with increasing values of x signify this. It does not seem desirable, however, to relate each value of D with the concentration obtaining at point x ; it would seem preferable to approach the true value of D for particular concentrations by keeping

the concentration difference between c and c_0 as small as possible. The variation of D with concentration has been rather generally disregarded in work on solid diffusion, and the published values must usually be taken as values for concentrations intermediate between the concentrations c and c_0 quoted.*

Matano¹⁹⁵ modified equation 2 to the form

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \quad [6]$$

which explicitly provides for a variation of D with c , and gave a solution for the experimental conditions stated in introducing equation 5. To solve this equation some assumption must be made regarding the variation of either c or D ; Matano assumed that c is some function of $\frac{x}{\sqrt{t}}$ and obtained a solution which permitted him to calculate a single value of D for the opposed diffusion of solute and solvent at every concentration. From the data of Grube and Jedelev¹⁰⁷ shown in Fig. 2 he produced a curve of D versus concentration, shown in Fig. 3. Matano placed the position of the diffusion interface on the c - x graph (Fig. 2) so as to show an equal number of atoms of Cu and Ni having diffused on either side¹⁵⁴. This seems to be wholly justified for substitutional solid solutions since an unequal transport leads to impossible consequences; Grube's¹⁰⁷ act in fixing the point arbitrarily at 50 per cent seems unwarranted. The selection of solutions of equation 2 on the basis of accuracy of fit with experimental data without regard to boundary conditions is an unjustifiable procedure, though this has been done²³⁻³¹. Attention to the proper fulfillment of boundary conditions is of prime importance; many penetration curves cannot be used to calculate diffusion coefficients because of uncertainty in the nature of the boundary conditions particularly as they apply to concentration and because of phase changes which cannot be adequately treated in a mathematical way^{105, 108, 109}.

Certain special techniques require particular note. Dunn^{41, 70, 71} determined D for the diffusion of Zn in α -brass by vaporizing the Zn in a vacuum and measuring the weight loss. Dunn assumed that the concentration of Zn at the surface was zero and that the rate of diffusion of Zn to the surface alone controlled the rate of loss of Zn (i.e., not the rate of evaporation). Some uncertainty attends this method, owing to the shrinkage of the sample and the resultant displacement of the surface "interface"; cracking of the surface during dezincification probably also affects the calculated diffusion coefficients^{79, 274, 284}, though Dunn's values agree well with those measured in other ways. The determination of the diffusion of C or N in Fe by reaction with carburizing or nitriding

* Nernst early recognized the variation of D with concentration in liquid systems.²⁰⁷

gases, or by removal of these elements by reaction with decarburizing or denitriding gases²³⁻³¹, involves a similar assumption of a rate of reaction (carburizing or decarburizing) at the surface relatively instantaneous compared to the rate of diffusion within the solid metal; in some cases

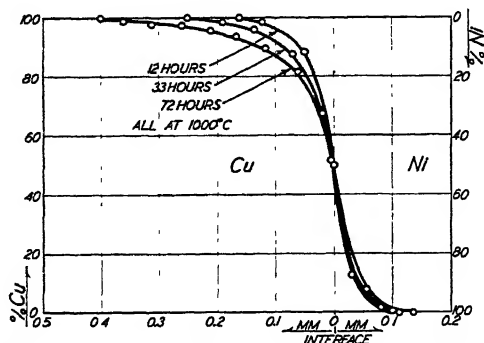


FIG. 2.—PENETRATION CURVES, COPPER AND NICKEL, SHOWING COMPOSITIONS AT DIFFERENT DISTANCES FROM THE INTERFACE¹⁰⁷.

proof of this would be welcome. The work of Brower, Larsen, and Schenck³⁶ is an interesting example of the determination of the rate of diffusion (of O in γ Fe) from the rate of removal of the diffusing element by reaction with H at the surface. It will be evident that these methods

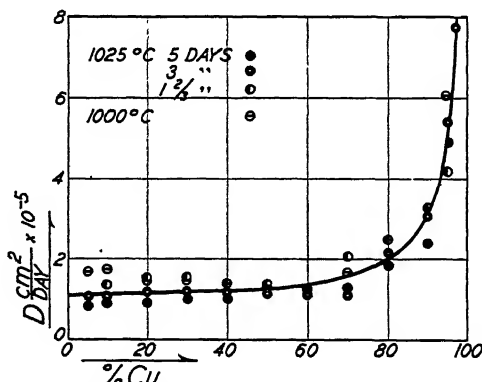


FIG. 3.—PLOT OF DIFFUSION COEFFICIENT AS A FUNCTION OF CONCENTRATION FOR THE COPPER-NICKEL SYSTEM¹⁹⁶.

will be of little use in a minute analysis of the effect of c upon D , for which concentration-depth curves are most useful.

The radioactive isotope technique (see many papers by von Hevesy and Seith) is a special technique,* as also the thermion-emission tech-

* The development of many artificially radioactive elements greatly extends the possibilities of this technique; at present the technique is limited to Pb, Tl, Bi and their alloys.

nique¹⁸¹, both of which will be mentioned later. These possess no obvious limitation, and are usually applied to small concentrations of solute.

Methods which depend upon averaging, such as those in which the changes in electrical conductivity^{7,35,39,92} or in lattice parameter^{192,193} accompanying diffusion in samples built up by alternate electrodeposition of two diffusing metals are measured, are of uncertain validity, for the results are not in agreement with those with more orthodox methods¹³⁷.

Any method which will determine concentration may be applied in determining concentration-depth curves and thus the diffusion coefficient. Simple chemical (or spectroscopic) analysis is ordinarily used and is to be preferred, but an X-ray determination of lattice parameter is satisfactory, particularly in systems where the parameter changes sharply with concentration. Special methods in which single concentrations (and the corresponding values of x) are determined, for example, by the use of X-rays on the outside of a diffusing couple, or by the use of a predetermined corrosion resistance limit^{86,156}, are accurate but do not give the full concentration-depth curve and therefore do not furnish information on the variation of D with c . Relatively few published diffusion coefficients are trustworthy; those which seem reasonably beyond criticism are assembled in Table 1.

It will be evident to metallurgists that the intimacy of contact at the interface between two diffusing bodies is of great importance in determining the degree of penetration, particularly when penetration is obtained by annealing a metal packed in a powder³, as in chromizing, or when bimetal strip is formed¹⁰¹. Any impediment at the interface—oxide films however thin, when these are not immediately dissolved during the diffusion anneal, or slag particles—will act to diminish the apparent interfacial area (factor A in equation 1), giving a degree of penetration and a calculated diffusion coefficient incorrectly low (Fig. 4). The recent comprehensive work by Bardenheuer and Müller¹⁴ on diffusion from sprayed metal coatings illustrates this; the presence of a reducing agent or a flux will assist in counteracting the impeding effect of oxide or slag, though of course fluxing alone will only partially counteract the effect. Generally actual atomic contact is required to obtain atom transfer, but this is not always easy to obtain; electrodeposition is the most generally useful method when care is taken with respect to

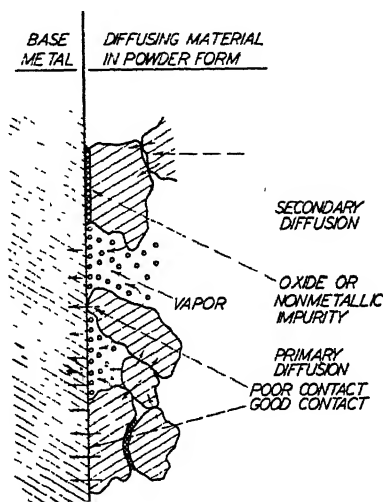


FIG. 4.—DIAGRAM SHOWING FACTORS AFFECTING DIFFUSION FROM A METALLIC POWDER INTO A MASSIVE METAL.

intervening oxide films, but the method is not always applicable, particularly when diffusion from one alloy to another alloy is desired. When the diffusing metal possesses a sensible vapor pressure, atom transfer is facilitated by transfer through the vapor phase, and doubtless this mode of transfer operates in many unsuspected cases though it does not seem likely, as it has been claimed, that transfer through the vapor phase is essential for all diffusion processes—certainly diffusion in alloys during homogenization or during decomposition proceeds without the intervention of a gaseous phase²⁵³. Mechanical methods, in which two surfaces are brought into intimate contact by rolling or drawing, have been too little used^{20,42,57,147}, for they offer a special advantage in fragmenting and attenuating oxide barriers.

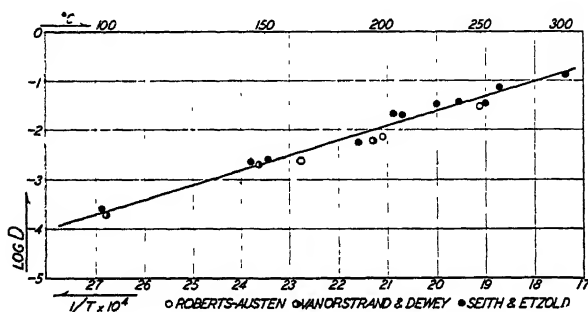


FIG. 5.—DIFFUSION OF GOLD INTO LEAD.

The diffusion coefficient varies greatly with temperature. This variation may be represented by an exponential expression

$$D = A \cdot e^{-\frac{b}{T}} \quad [7]$$

where T is the absolute temperature and A and b are constants.* In logarithmic form this becomes

$$\log_e D = \log_e A - \frac{b}{T} \quad [8]$$

which is linear, giving a straight line when $\log_e D$ is plotted against $\frac{1}{T}$ whence b is the slope. This is clearly shown by the data on the diffusion of Pb in Au, Fig. 5. All diffusion data in metal systems obey this law,†

* Exponential relationships were proposed by von Hevesy in 1920¹²⁵, by Tammann and Schönert in 1922²⁸⁶, and by Weiss in 1923²⁸⁵, but the form given is a simplified form of the equation proposed by Dushman and Langmuir⁷⁶ in 1922, to be discussed later.

† Owen and Pickup have produced similar equations for the interdiffusion of mixed metal powders^{211,212}.

though the data may be held insufficiently complete and restricted to a too narrow temperature range to be wholly satisfactory on this point.*

PHYSICS

Inasmuch as diffusion consists in an interchange of atoms between two crystal lattices, the mechanics of the process must involve crystal lattices and their energies. Several theories have been proposed to provide a picture of the necessary atom transfer. Rosenhain²²⁴ postulated concomitant slip in such a way that adjacent crystal blocks are displaced and the atoms once neighbors on an atom plane become far separated, but this picture does not seem to provide the necessary uniform migration and there is no experimental evidence supporting it. Frenkel⁵⁸, in an endeavor to avoid difficulties which might arise on the basis of simple interchange on lattice positions, proposed that atoms should "dissociate" from lattice positions and become mobile in interstitial space, ultimately again "associating" with new lattice positions; Smekal²⁴⁸ has proposed that atoms can migrate only into interstices and particularly into lattice imperfections or mosaics, and has set up a number of discrete processes which in their summation give general intralattice transfer, but—as we shall see more in detail later—the function of mosaics in diffusion is extremely uncertain. Langmuir^{148,224}, on the other hand, has proposed a simple cyclic interchange of atoms, involving atom interchange on lattice points, and Braunbeck³³ (cf. ref. 248) derived a theory to explain the electrical conductivity of salts on the basis of a simple atom interchange on lattice points. It seems unnecessary at the moment to go beyond this picture to explain the rather limited data now available.

The vibration of atoms about mean lattice positions with a distribution in frequency and a limiting maximum frequency and with amplitudes and thus energies increasing with temperature, gives the necessary dynamic basis for atomic mobility. Dushman and Langmuir⁷⁶ assumed from the analogous treatment of chemical reaction rates⁷² that an atom must possess a minimum energy E before it can surmount the surrounding potential barrier and that the probability of a change in place of a single atom (in the analogous case of chemical reaction rates, the probability of reactive collision) is proportional to

$$e^{-\frac{E}{kT}} \quad [9]$$

where k is the Boltzmann constant. For a gram-atomic weight, this becomes

$$e^{-\frac{Q}{RT}} \quad [10]$$

* Data on the related electrical conductivity of solid salts indicate a dependence of A on T , but there is no indication of this for diffusion in metallic systems²⁴⁸.

where R is the gas constant and Q is the energy for transfer of a gram-atomic weight.* Following this reason Dushman and Langmuir⁷⁶ proposed a general diffusion equation:

$$D = \frac{Q}{Nh} \cdot \delta^2 \cdot e^{-\frac{Q}{RT}} \quad [11]$$

Q is then designated as the heat of diffusion, analogous to the heat of activation in chemical reaction, N is Avogadro's number, h is Planck's constant, δ is the interatomic distance (the "jump distance"), and the other quantities as given above.† Equation 11 is often simplified to

$$D = A \cdot e^{-\frac{Q}{RT}} \quad [12]$$

which is another form of equation 7.

An extensive test of equation 11 is embarrassed by the paucity of trustworthy diffusion coefficients. We note, however, that in every case the best data are quite in accord with the expression, with the exception of systems of noncubic metals²⁴⁸ to which the equation does not apply. Table 1 lists the values of Q derived graphically from the plot of the logarithm of the diffusion coefficient against the reciprocal of the absolute temperature, as in Fig. 5 (the slope is Q/R), and in another column gives values of Q calculated from equation 11 from a single diffusion coefficient at a single temperature; the similarity of the derived and calculated values is a test of equation 11. Only when diffusion data are questionable are the departures great. The applicability of the equation is not limited to substitutional solid solutions, where diffusion can occur only by interchange of lattice positions, but extends as well to interstitial solid solutions (C in γ Fe) where diffusion occurs by simple penetration into interstices. This latter result is somewhat surprising in view of the radical difference in modes of atom transfer in the two types of solid solution. Although a general validity can hardly be claimed for the Dushman-Langmuir equation in view of the meagerness of good data, it is difficult not to be fascinated by its possibilities, both scientific and practical.‡ An inspection of the equation shows that a single diffusion coefficient at one temperature suffices for a calculation of Q , since all other quantities are known constants (the value of the interatomic distance δ for the solid solution may

* Joffé¹⁵⁰ gave this treatment in 1923 and Braune²⁴ also in 1924.

† The newer type of argument, based on wave mechanics, as recently elucidated by Guernsey and Condon¹¹⁰ and by Bitter¹⁸, in which an atom paradoxially has a finite probability of piercing a potential barrier even though its energy is inadequate, leads to a similar treatment of diffusion phenomena.

‡ Von Hevesy¹³⁰ has compared the data on diffusion in salts with the Dushman-Langmuir equation. Jost¹⁶¹ has recently questioned the applicability of the quantity

$\frac{Q}{Nh} \cdot \delta^2$ to inorganic salts.

TABLE 1.—*Applicability of Dushman-Langmuir Equation to Diffusion Data*

Solvent	Solute	Q	
		From Diffusion-temperature Curve	From Dushman-Langmuir Equation
Cu	Zn (9.58%) ⁷⁰	41,700	41,000 ^a
	Zn (29.08%) ⁷	41,700	38,000 ^a
	Sn (10%) ¹⁹⁶	40,200	40,000
Pb	Pb (self-diffusion) ²³⁰	27,900	24,400
	Sn ²⁴⁴	24,000	23,200
	Tl ²⁴⁴	21,000	22,380
	Bi ²⁴⁴	18,600	21,900
	Cd ²³⁸	18,000	19,970
	Ag ²⁴⁴	15,200	15,700
	Au ^{220-222, 210, 237}	13,000	13,300
Ag	Au ¹⁸⁶	57,600	57,000
W	Th (small W grains) ⁸⁵	94,000	96,700
	Th (large W grains) ⁸⁵	94,450	118,200
	U ⁷⁵	100,000	100,500
	Ce ⁷⁵	83,000	82,700
	Zr ⁷⁵	78,000	77,400
γ -Fe	Yt ⁷⁵	68,000	70,100
	N ²⁴	34,600	38,100
	C ²¹³	36,000	36,700

^a Dunn's calculation of Q is incorrect through confusion in the use of units; the correct values are given in the table.

be found in tables or approximated from the values for the pure component metals); with Q determined, D may be calculated for all other temperatures. Thus processes like carburization and homogenization can be treated over a range of temperatures on the basis of studies at one temperature only. Furthermore, if D and Q are both known, δ can be calculated, at least approximately.

Associating the rate of atom interchange with energies of activation much in the manner of Dushman and Langmuir, Braune³⁴ correlated these energies with the Lindemann theory of melting and derived an expression for the diffusion coefficient:

$$D = A \cdot e^{-\frac{3b^*T_s}{T}} \quad [13]$$

where b is a constant with values between 1 and 2 for the different metals, T_s the absolute temperature of melting, and A a constant. Van Liempt^{183, 184} extended this treatment and calculated the "jump time" and the fraction of atoms changing place in one second, and also the number of oscillations performed by a single atom before changing place. He deduced the equation

$$D = \frac{8}{3\pi} \cdot \nu \cdot \delta^2 \cdot e^{-\frac{3b^2 T_e}{T}} \quad [14]$$

in which ν is the characteristic (monochromatic) frequency. Thus ν can be calculated from D , in agreement within an order of magnitude with the value of ν deduced from the Lindemann equation.* An equation developed by Polanyi and Wigner²¹⁶ is quite similar to the Dushman-Langmuir equation. The development of these various equations is rendered difficult by the incompleteness of the physical theory of the metal lattice, and by the lack of a sufficiently large body of good experimental data on diffusion.†

SELF-DIFFUSION

The simplest type of diffusion is self-diffusion, that is, diffusion of atoms within their own lattice. A technique to determine the self-diffusion coefficient was developed by von Hevesy^{102, 103, 131, 136, 239}, consisting in inoculating the surface of Pb with a radioactive Pb isotope ThB, and following the diffusion of the isotope inward by a simple measurement of the surface radioactivity of the sample with an electroscope, for the radioactivity decreases as the ThB diffuses away from the surface; the diffusion coefficient is then calculated by the method developed by Fürth⁹⁰.‡ The values obtained are shown in Tables 1 and 2.

RATES OF DIFFUSION

Many of the ideas now applied to diffusion in solid metal systems originated in the work of Tubandt, Joffé, Jost, von Hevesy§ and others on the electrical conductivity of solid inorganic compounds. It has been shown that the electrical conductivity of quartz^{150, 294} and particularly of salts such as PbI_2 is wholly or partly electrolytic in character⁵², accompanied by an ion transport with the conductivity proportional to the rate of diffusion of the conducting ion or ions. Thus we may represent the change in electrical conductivity with temperature by an equation similar to equation 12 where the conductivity λ replaces D and the constant A

* Van Liempt applied his methods to recrystallization, which, like diffusion, depends on atom mobility and thus upon energy states¹⁸³. Tammann's work^{260, 263, 267} on the sticking of powdered metals on heating is similarly related to diffusion.

† Several workers have tried to demonstrate the effect of pressure on the rate of diffusion⁵⁴, but unsuccessfully^{210, 237}; it is possible that very high pressures will be required to demonstrate this effect—a combination of Bridgman's technique for high pressure and the radioactive technique for measuring diffusion should give positive results.

‡ This method has also been used to determine the rate of self-diffusion of Pb ions in solid salts^{131, 132, 133}. When recoil rays are used, values of D down to 10^{-12} sq. cm. per day may be measured.

§ See references under these names in bibliography; see also summaries by Smekal²⁴⁸ and by Douglas-Clark⁵²; cf. refs. 276–283.

becomes a different constant. Such an equation will apply to the case where only one ion is mobile, as in αAgI , αCuI , etc. When both ions are mobile two exponential terms are required, each with its own characteristic values, as for PbI_2 at temperatures not far below the melting point, for which we have^{132, 133, 234}

$$\lambda = 9.70 \cdot 10^{-4} \cdot e^{-\frac{8760}{RT}} + 1.5 \cdot 10^{-5} \cdot e^{-\frac{30000}{RT}} \quad [15]$$

The Q value in the electrical conductivity or the diffusion equation represents the energy necessary to "loosen" a gram-atomic weight from the lattice and thus render it mobile. This loosening doubtless originates in the thermal vibrations, but it has been suggested particularly by Fajans⁸⁰ and von Hevesy^{129, 130} that the normal polarity of such ionic lattices is partially neutralized, and the electrostatic lattice forces therefore diminished, by the increasing number of close approaches of the vibrating ions and the resultant interpenetration of electron shells; this represents a loosening of the lattice, dependent upon the inherent polarizability and deformability of the ions concerned. The degree of loosening is high when the deforming power of the cation and the deformability of the anion are high, that is, when the electron affinity of the cation is great and that of the anion small, as with AgI ; the mobility of Ag in its salts increases as we pass from the nitrate through a series of decreasingly strong anions to the telluride¹³⁰. Since all molten salts are completely loosened, we may expect little difference in their electrical conductivity, and this is observed; but the degree of loosening in the solid state varies within wide limits. As a qualitative measure of the amount of loosening in a given solid we may take the ratio of the electrical conductivity above and below the melting point—when this ratio is large, the solid is little loosened, and when small it is greatly loosened. In the case of αAgI the solid is so greatly loosened that its electrical conductivity is actually 10 per cent greater than that of the melt, but with markedly polar salts, the ratio is very large, as with NaCl where the ratio is 10^5 .

The relationships observed in alloys seem to be consistent with this point of view. Although the effect of alloy formation and particularly of solid solution formation upon the distribution of valence electrons and the state of ionization and deformation is extremely difficult to study, it is of course well known that such effects exist. The classic work of Kremann¹⁷³ on the electrolysis of liquid alloys and the recent work of Seith on the electrolysis of solid alloys is direct experimental evidence of partial ionization in alloy systems.* The experimental data on diffusion

* Seith and Kubaschewski²⁴⁵ have shown that solid solutions of C in γFe , Au in Pb, and Au in Pd may be electrolyzed, with C surprisingly passing to the cathode, and Au in both cases to the anode¹⁶².

in alloys of Pb are most instructive. The rate of self-diffusion in Pb above the melting point is much more rapid than below the melting point—the ratio is 40,000—and the lattice is thus very little loosened. Since the electronic structure of ThB is known to be identical with that of Pb, the diffusion of ThB is accompanied by no special chemical effects. When Sn diffuses in Pb, however, its atoms move in a lattice of atoms of slightly differing chemical nature, and chemical affinity effects obtain—atom polarization and deformation—resulting in a loosened lattice, and correspondingly higher values of D and lower values of Q . These effects will become more marked as the chemical difference increases as shown clearly by the data of von Hevesy and Seith^{134,135,233,242,244} given in Table 2, and shown in Fig. 9.

TABLE 2.—*Diffusion of Metals in Lead*

Metal	Au	Ag	Cd	Bi	β -Tl	β -Sn	Pb Self-diffusion
D , cm. ² sec., at 285°C.	$4.6 \cdot 10^{-8}$	$9.1 \cdot 10^{-8}$	$2 \cdot 10^{-8}$	$4.4 \cdot 10^{-10}$	$3.1 \cdot 10^{-10}$	$1.6 \cdot 10^{-10}$	$7 \cdot 10^{-11}$
Q	13,000	15,200	18,000	18,600	21,000	24,000	28,000
Crystal system of solution	f.c.c.	f.c.c.	c.p.h.	rhomb.	f.c.c.	tetr.	f.c.c.
Maximum solid solution, atomic per cent	0.05	0.12	17	35	79	29	100
Atomic radii, Å.....	1.44	1.44	1.52	1.82	1.71	1.58	1.74
Melting points, deg. C	1063	960	321	271	303	232	327

We may note that the rate of diffusion increases and the heat of diffusion decreases as the various diffusing elements become chemically more and more different from Pb* and that the solid solubility decreases (though not quite consistently); the difference in melting points increases and the atomic radii become less.

F. N. Rhines²⁰⁴ has recently shown that the rates of diffusion in the α solid solutions in the systems Cu-Sn, Cu-Si, Cu-Al, and Cu-Zn decrease in the order stated; that is, decrease with increasing chemical similarity of the two diffusing elements. This attack, including diffusion in the structurally analogous system of Cu, Ag and Au with the elements of the B subgroups, appears to be particularly attractive, especially in view of the relationships recently discovered by Hume-Rothery^{145,146} between valence electron concentrations and liquidus and solidus temperatures, and in view of the increasing knowledge of metal classification¹⁴⁶ and of the thermodynamic treatment of solid solutions²⁴⁶.

When the Pb lattice is loosened by foreign atoms in solid solution, the rate of self-diffusion is increased. Thus, the Au atom is small and retains

* Graham¹⁰⁰ noted as early as 1861 that high values of D are ordinarily associated with slight changes of D with temperature for diffusion in aqueous solutions; i.e., with low Q values.

its valence electron strongly; when alloyed with Pb, the atoms of which are large and show less electroaffinity, the Pb lattice is loosened and the rate of self-diffusion increases¹³⁴. Similarly, the mobility of Ag is increased by alloying with Sn¹³⁰.

The relation between melting point and D and Q are of particular interest. Equation 13 was developed by Braune to provide a quantitative statement of this relationship. Braune considered that the melting points could be taken as corresponding temperatures for the comparison of diffusion data when the melting points are not too nearly equal. Von Hevesy has approximated the self-diffusion coefficients in the elements Ag, Au, and W¹³⁵,* which, together with the measured value for Pb, show diffusion coefficients at a constant temperature in inverse relation to the absolute melting points.

In binary systems it has been observed that the diffusion coefficients in either terminal solid solution are the greater in the solid solution with the lower melting point; thus the diffusion coefficient of Au in Pb is 26,000 times that of Pb in Au¹³⁴.† The metallurgist will note that the solid solubility in a binary system is usually the greater in the metal with the higher melting point, and would thus expect that diffusion rates in such systems should increase as the melting points become more divergent and as the solid solubility becomes less. The relationship between melting point and diffusion coefficient is borne out by the studies of Jost¹⁶⁰ on the systems of Ag and Au with Pt and Pd, roughly by the studies by Matano on the systems Pd-Cu, Pd-Ag, Pd-Au¹⁹⁴, and particularly by the studies of Jedelev^{147,194} on the systems Au-Pt, Au-Pd, and Au-Ni, in which the greatest difference in D with changing concentration occurs in the system Au-Ni where the melting points of the component metals have the greatest difference. The recent work by Sen²⁴⁷ may be interpreted in the same way. Fig. 3 illustrates this relationship for the system Cu-Ni.

The effect of melting point is also shown by the recent work of Seith and Keil²⁴³ in which it is demonstrated that Bi, which lowers the melting point of Pb, increases the rate of self-diffusion whereas Tl, which raises the melting point, does not increase it; these workers showed that Dunn's⁷⁰ data on the rate of diffusion of Zn in α brass of different composition (and

* These approximations were made from data on binary isomorphous systems on the assumption that D for systems composed of metals very similar chemically should not differ greatly from D for self-diffusion.

† Keil¹⁶⁸ infers from his work on the diffusion of Au and Ag in Pb that the solid solutions formed are interstitial and that this accounts for the high values of D observed, since the solid solution of C in γ Fe is interstitial and exhibits a high diffusion coefficient. This seems unlikely; an attempt²⁰⁴ to determine the nature of these solid solutions by a precision measurement of a_0 on quenched alloys failed presumably because of the very low solid solubility. Thompson and Dearden²⁷² from observations on diffusion in Au-Ag alloys have incorrectly inferred that these alloys are interstitial in nature.

different melting point) can be reduced to a common rate of diffusion when the data are compared at corresponding reduced temperatures.

We may conclude, then: (1) that the rate of self-diffusion at a given temperature is the lower the higher the melting point of a metal; (2) that in a series of alloys with a common base metal, such as the lead alloys described above, the rate of diffusion is the greater the higher the melting point of the diffusing metal; and (3) that in a binary system the rate of diffusion is the greater in the lower melting metal.

When, however, the melting points in a binary system are not greatly different, as in the system Cd-Pb, atom polarization seems to be the determining factor and, disturbingly, large differences in diffusion coefficient may appear. Diffusion in metals of low symmetry with low coordination numbers appears to be less rapid than in cubic metals⁵⁵, and in this case purely symmetry relationships appear to exercise an effect^{129, 130, 134, 135, 143}.

It appears, then, that high diffusion coefficients are associated with large differences in melting points, large differences in atom size, and with low degrees of solid solubility modified in some fundamental way by polarization properties and resultant distortion and asymmetry, but as in similar attempts at correlation among the factors affecting solid solubility, the true form of this relationship has escaped exact statement.

The effect of third elements upon the rate of diffusion offers interesting possibilities. It has been stated several times that Cr will not diffuse into Fe from a powder at temperatures below 1100° C. unless Si is present¹⁴; it is not clear that this is a third element effect, for it is possible that Si operates here as a deoxidizing agent. Grube¹⁰⁷ noted that 0.5 per cent Mn in Ni decreased the rate of diffusion of Cu into Ni to one-quarter of the value for pure Ni, and though the grain size was larger in the Mn-bearing Ni, which might explain the lower diffusion rate, a third element effect may be present; whatever the origin, the effect is marked and may be of use in considering the homogenization of cupronickel castings. Inasmuch as third elements, when present in sufficient quantity, will greatly modify the lattice characteristics, such as the dimensions of the unit cell, an effect from this source might be readily predicted.

The effect of smaller percentages of third elements, however, is surprising. Grube¹⁰⁹ found the rate of diffusion of W into vacuum-melted electrolytic Fe to be four times greater than ordinary electrolytic Fe; Yamauchi²⁹⁹ found Pb, Sn, Zn, Fe, to increase the rate of diffusion of Zn in α brass and Mn to decrease it. Tammann and Schönert²⁶⁸ found the rate of diffusion of C into γ Fe to vary with the purity of the Fe, as did Bramley²³⁻³¹. Bramley²⁵ and his coworkers found many surprising effects, among which we may mention that O decreases the rate of diffusion of C in γ Fe, as does S, that C decreases the rate of diffusion of P, and surprisingly that O increases the rate of diffusion of N. Fry⁸⁹ states that

P and S diffuse more readily in γ Fe when present simultaneously than when present separately. Mrs. Freche⁵⁷ states that simultaneous diffusion of Mg and Si in Al takes place in the ratio given in the compound Mg_2Si rather than according to the normal separate diffusion coefficients.

It is possible that some of these variations may have been caused by the effect of third elements on grain size, for this possibility has been rather generally disregarded. This matter should be investigated comprehensively, for it may afford important results for the technique of surface improvement, particularly carburizing and nitriding, for homogenization treatments, and indirectly—as we shall see—for controlling rates of reaction in the solid state.

METALLOGRAPHY

The requirement that solid solutions must obtain if diffusion is to occur—as proposed by Guillet¹¹⁶ in 1914 though implicit in earlier work—leads to a number of simple yet important and useful metallographic principles.* Two metals will diffuse into one another with the formation of alloy layers equal in number to the phases stable in the binary system at the chosen temperature. The rapidity with which these layers form will vary from layer to layer and from system to system according to the respective diffusion coefficients.†

Thus Cu brought into conjunction with Zn vapor at 400° will form layers of α , β , γ , ϵ and η brass as shown by Elam⁷⁹; the ϵ phase, and the γ also are brittle and tend to break off on polishing—this, together with the difficulty in etching these phases differentially, make their recognition in such a sample difficult, so that only the α , β and γ phases can be seen in Fig. 6. Such alloy layers have been found in annealed Cu-plated Zn-base die castings and appear even after “annealing” at room temperature^{47,217}; Rigg²¹⁹ has shown that four alloy layers will develop on heating the couple Fe-Zn at temperatures 100° below the melting point of Zn. Using this technique Hudson¹⁴³ showed that the β phase in the Cu-Zn system forms on diffusion below 470°C . and is thus a stable phase below this temperature; in a similar way the present uncertainty in the continuity of the phase fields in the Al-Zn system²³⁰ could be readily clarified. Obviously, then, diffusion cannot occur in phases which have no range in solid solubility, and this may be used as a test for solid solubility, as Hume-Rothery¹⁴⁴ has done. It is not an easy matter to

* Countless interesting observations on diffusion have been made which can hardly be summarized. Desch has collected many of the earlier observations into an interesting review⁶⁴ published in 1912.

† Very little work has been reported on the rate of diffusion in intermediate alloy layers; Köhler¹⁷¹ reports that Zn diffuses in β brass more rapidly than in α . The relative widths of the various alloy layers in systems showing intermediate phases are in need of quantitative determination and analysis, though Tammann and Rocha²⁶⁵ studied this point briefly and Heindlhofer and Larsen¹²⁴ touched upon it.

determine the composition of diffusion layers, though in a qualitative way the method is more useful in the study of the constitution of metal systems than has been generally appreciated. Within each diffusion

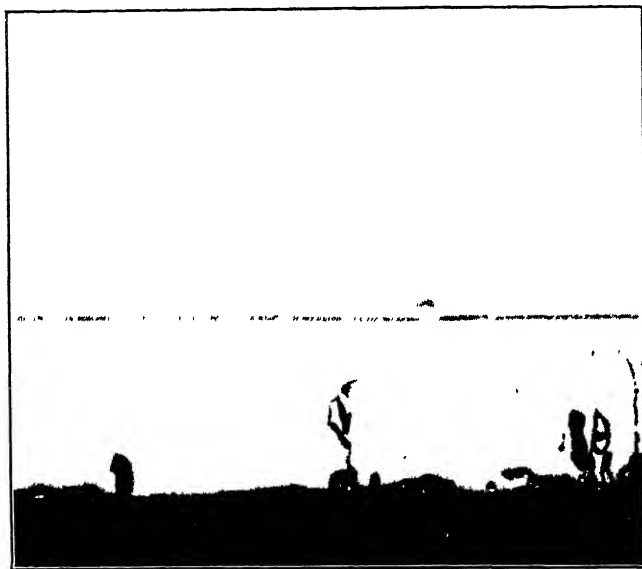


FIG. 6.—PENETRATION OF ZINC INTO COPPER²⁰⁴.

Cu packed in Zn powder; held 150 hr. at 400°; quenched. Unetched, $\times 50$. Showing α phase at top, β phase in narrow band near center, white γ phase at bottom.

layer the full concentration range of the solid solution obtains; at each interface between alloy layers there is necessarily a discontinuous change in composition corresponding to the extent of the intervening heterogeneous range. The diffusion curve for Cr in γ Fe shown in Fig. 7,

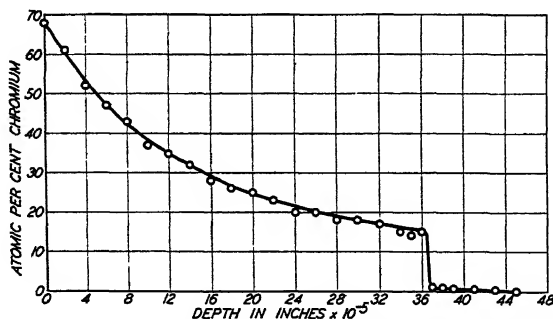


FIG. 7.—DIFFUSION PENETRATION CURVE FOR CHROMIUM IN IRON, 96 HR. AT 1200°¹³⁷.

obtained by Hicks¹³⁷ from a determination of the lattice parameter, illustrates this, where the discontinuity corresponds to the α - γ interface at the temperature of diffusion. It is an interesting fact, as Elam⁷⁹ has

shown, that orientation relationships obtain across such interfaces, similar to those in the closely analogous case of crystalline overgrowths, or in oxide films on metals²⁰⁰, and of course quite similar to those displayed in Widmanstätten figures.*

These facts present a simple method for the determination of the extent of terminal solid solubility, for evidently a pure metal can absorb by diffusion only the amount of solute that it can take into solid solution. This simple method of establishing solid solubility has much to recommend it; using it, Seith and Etzold²³⁷ determined the very slight solid solubility of gold in lead, and Ziegler³⁰¹ studied the solubility of oxygen in solid iron.

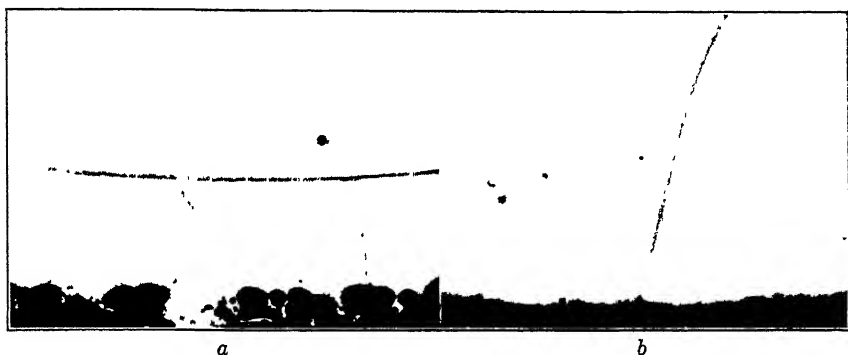


FIG. 8.—DIFFUSION OF CHROMIUM INTO IRON.

a, above A_2^{204} . Hydrogen-treated carbonyl Fe packed in Cr powder; held 70 hr. at 1000° ; quenched. Showing phase interface (horizontal dark line), with columnar crystals of α phase at bottom and with (what had been) γ phase at the top.

b, below A_2^{204} . Hydrogen-treated carbonyl Fe packed in Cr powder, held 200 hr. at 850° ; quenched. Showing no phase interface and no columnar crystals.

Etching: Aqua regia, then picric acid. $\times 100$, reduced $\frac{2}{5}$ in reproduction.

The diffusion of one metal into another when accompanied by the generation of a new phase leads to the formation of columnar grains. This has now frequently been shown; the earliest explanation of this phenomenon appears to be that of Green¹⁰⁰, advanced to explain the phenomenon as it occurs in the decarburization of austenite between the A_1 and A_3 temperatures, and reiterated later by Jeffries, Hultgren and Benedicts in discussing a paper by Kelley¹⁷⁰: namely, that the first nuclei of the new phase formed on the surface grow inward by progressive absorption of the underlying crystals of the original phase much as

* It seems possible that the orientation relationships in diffusion layers may be identical with those in Widmanstätten figures pertaining to the same phases; E. L. McCandless²⁰⁴ has shown that the orientation relationship between FeO and the Fe_3O_4 phase formed on decomposition (which is an intergrowth, a Widmanstätten figure) is identical to that obtaining between Fe_3O_4 and the FeO grown upon it by reduction (an overgrowth).

columnar crystals grow from the liquid state on freezing^{2,5,13}. This explanation seems incontestable; columnar crystals may originate, however, in other ways, particularly in the decarburization of steel in which some effects of obscure origin have been noted, as discussed recently by Rowland and Uptegrove²²⁶. Thus the diffusion of Cr into γ Fe^{169,170} results in the formation of columnar α crystals, as shown in Fig. 8a; when, however, this diffusion occurs below A_3 , when no new phase is formed, columnar crystals are not generated, as shown in Fig. 8b. When the diffusing element lowers instead of raises A_3 , columnar crystals will appear at temperatures below A_3 but not above A_3 ¹⁵³. Although some uncertainty has been expressed, this behavior seems to be general and without exception. The formation of such columnar grains as well as the presence of a sharp interface is proof of a phase change; in the absence of a phase change the term "diffusion zone" (Fig. 8b) is improper, for there is no sharp limit of penetration but only a gradual decrease in concentration with increasing depth.

ANISOTROPY

The success of generalized diffusion equations (equations 11 and 14), which include a factor for the distance between lattice points and which imply that diffusion proceeds by a process of discrete jumps from one to another of these points, suggests definitely that diffusion in the solid state depends for many of its features upon the geometry of the crystal lattice, and this has been found to be true. Excluding for the moment all extraneous effects we may profitably consider diffusion within the single crystal or grain. From this point we may develop our discussion to the polycrystalline aggregate, including a discussion of grain boundary and surface effects and of distortion effects.

It has been found that the magnitude of the electrical conductivity of PbI_2 and $PbCl_2$, and therefore the diffusion coefficient, is dependent upon the crystallographic direction measured²³⁴ (it was observed many years ago that the conductivity of quartz shows a similar dependence^{150,294}). At 326° C. the conductivity of PbI_2 parallel to the c -axis is $\frac{1}{30}$ of that perpendicular to this axis; the lattice is a complicated noncubic layer lattice²³⁴.*

A similar variation in the rate of diffusion with crystallographic direction, that is, a similar anisotropy, has been observed for self-diffusion in rhombohedral Bi²³⁴. Although it might be argued that the sensitive structural nature of Bi and its mechanical fragility may rob the experi-

* Self-diffusion coefficients of Pb in PbI_2 and $PbCl_2$ using ThB have been measured by von Hevesy and Seith^{132,133}; it has been found that the ion with the smaller Q value (I and Cl) shows the greater variation with direction²¹⁴; the Pb ion shows no dependence upon orientation^{132,133}.

ment of some of its reality as applying to a true single crystal, an anisotropy in diffusion is to be expected owing to the low symmetry of the lattice. Fig. 10 shows the measurements of Seith²³⁴. The rate of diffusion at 269° C. perpendicular to the rhombohedral axis is greater than that parallel to the same axis by a factor of approximately one

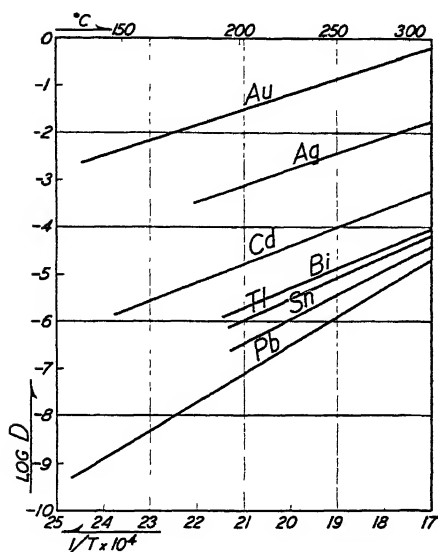


FIG. 9.—DIFFUSION OF VARIOUS METALS INTO LEAD²⁴².

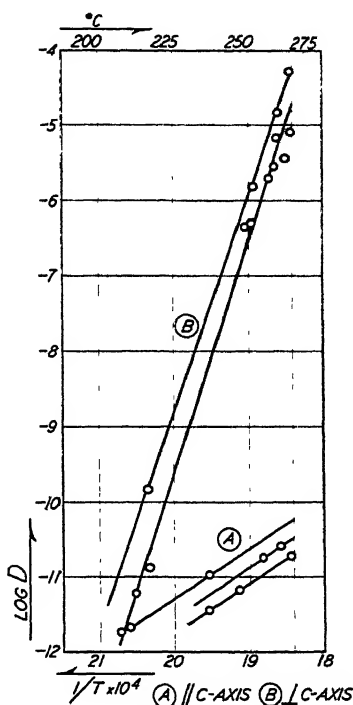


FIG. 10.—SELF-DIFFUSION IN BISMUTH²³⁴.

million.* This is the only example now available for anisotropy in metal crystals, though it might be expected in all noncubic crystals.

Although the mechanism of diffusion seems to require the exchange of atoms in lattice positions, that is, a translatory movement along crystal directions, there is no resultant macroscopic anisotropy of diffusion in cubic metals. Elam⁷⁹ found that Zn diffuses into a single crystal of Cu equally along all directions and this result has been recently confirmed²⁰⁴.

* It has been pointed out²³⁴ that the difference in the coefficients of expansion in the two directions may in part account for the great differences in the slopes of the curves owing to the increasing separation in one direction as compared to the other, and that therefore the Q values may not have their orthodox explanation as activation energies.

Fig. 11 shows an equal penetration of Zn around the surface of a single crystal of Cu as judged by the width of the etching band. The diffusion of C into γ Fe in a coarse-grained sample of Fe was found by C. Wells²⁰⁴ to show an equal penetration in each crystal grain as judged by the depth at which the last trace of precipitated carbide could be noted, regardless of the orientation of the grain, Fig. 12; entirely similar results were obtained for the diffusion of N in α Fe, as shown in Fig. 13. The striking photograph presented several years ago by Dr. C. S. Smith²⁵¹ of Cu-Si alloys, the surface of which had been oxidized, shows oxygen penetration, as judged by the appearance of SiO_2 particles, to equal depths for every grain, independent of the orientations of the separate grains.

Although certain microstructural irregularities along the diffusion zone in samples showing a phase interface have been interpreted as

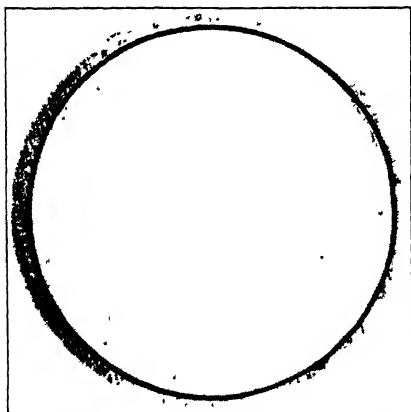


FIG. 11.—DIFFUSION OF ZINC INTO SINGLE CRYSTALS OF COPPER²⁰⁴.

Single crystals of Cu [the (110) face lies in the surface] packed in α -brass chips; held one week at 775°. Etching: Ammonia + hydrogen peroxide. $\times 5$; reduced $\frac{1}{2}$ in reproduction. Showing narrow black (stained) α phase; outside is mounting metal; inside is copper. Showing equal depths of zinc penetration.

evidence for anisotropy^{105,108,109}, the evidence is not weighty. From the evidence available we must conclude that the rate of diffusion in cubic crystals is independent of the direction measured. This seems rather contradictory to the supposition that atoms diffuse by jumps along preferred crystallographic directions, but calculation shows that cooperative movements along several directions of the same Miller indices give macroscopic isotropy rather than anisotropy²⁰⁴.*

DISTORTION

Much has been written about crystal mosaics and their effect on diffusion, especially by Smekal²⁴⁸⁻²⁵⁰. The increase in the rate of diffusion with temperature (as represented by the Q value in equation 11) represents a loosening of the lattice, as pointed out above. This conception of thermal lattice loosening has been extended by several writers, particularly von Hevesy, to include mechanical loosening originating in cold-work, and by Smekal with less justification to a supposed congenital loosening associated with lattice imperfections and mosaics. It is possible

* Joffé¹⁵² quotes data showing that the electrical conductivity of NaCl is isotropic, though reported earlier to be anisotropic; there are no trustworthy data indicating an anisotropy in the electrical conductivity of cubic salt crystals, and it seems quite unlikely that such an anisotropy exists.

that lattice imperfections may in some cases accelerate diffusion by the creation of quasi-grain boundaries when diffusion at grain boundaries is faster than within the grain, but there is at present no experimental basis



FIG. 12.—CARBURIZED COARSE-GRAINED IRON²⁰⁴.

Hydrogen-treated carbonyl Fe carburized at 950° for 20 hr. in dipentene + benzene + H₂; furnace-cooled at 10° per min. Etching: Picric acid in alcohol. Reduced $\frac{1}{3}$ in reproduction. Showing (in ink) several (former) γ -grain boundaries; showing equal depth of penetration in each grain and no grain-boundary penetration.

for the assumption of a special participation of periodic mosaic surfaces in the process of diffusion. Joffé¹⁵¹ doubts the importance of Smekal's contention, and Jost^{19,129} has shown that the electrical conductivity and



FIG. 13.—NITRIDED COARSE-GRAINED IRON²⁰⁴.

Hydrogen-treated carbonyl Fe nitrided at 525° for 30 hr. in NH₃; furnace-cooled at 10° per min. Etching: Saturated picric acid in alcohol. $\times 100$; reduced $\frac{1}{4}$ in reproduction. Showing nitrogen penetration from left; grain boundary lower middle left to right. Showing equal depth of penetration in each grain and no grain-boundary penetration.

the rate of diffusion of salt crystals are independent of thickness down to thicknesses less than that generally assumed for the mosaic period, and Jost¹⁵⁶ has also shown that the rate of diffusion in similarly thin (10^{-6} cm.)

layers of metals is as rapid as that in larger samples; in layers of such thicknesses the periodic plane is manifestly absent, and the phenomena must be those characteristic of the crystal without mosaic. Furthermore, the creation of homogeneous solid solutions by diffusion will sooner or later require that *all* portions of the lattice be penetrated, not only mosaic or imperfection surfaces. It seems, therefore, that the various *e*-functions proposed by Smekal²⁴⁸ to represent diffusion from lattice point to imperfection, along imperfection surfaces, etc., are unnecessarily complicated. The problem of imperfections in connection with diffusion is in the same uncertain state as that relating to the mechanical properties of crystals. At the present moment it seems preferable to gather good experimental data rather than to hypothesize at great length.*

It has been observed that the electrical conductivity of salt crystals is sensibly increased by cold-work²³⁴. Pressed powders and rapidly frozen (and thus strained) crystals of inorganic salts possess conductivities as much as fifty times greater than carefully prepared single crystals¹²⁸. There can be little doubt that cold-work can often increase the rate of diffusion, but this fact, together with the supposed necessity for imperfections, has led a number of writers to the belief that diffusion cannot take place in a strain-free ideal crystal, and even to the belief that diffusion cannot take place within a strain-free *real* crystal^{65-67,79}. This latter point is definitely incorrect, for diffusion has been observed in single crystals of metals as nearly strain-free as they may be made.

The metallurgist will immediately recognize the necessity for diffusion within the single crystal grain, for he has often observed the formation of a precipitate within a grain. Seith and Keil²³⁹ have shown evidently beyond dispute that self-diffusion occurs within single crystals of lead; it has been shown by others that Mo¹⁸⁴, C⁶, and Th^{181,85}, respectively, will diffuse in single crystals of W, and that H will diffuse through single crystals of Fe⁷⁸; it was shown some years ago¹⁹⁸ that N will diffuse rapidly into very large crystals of α Fe. Elam's⁷⁹ observation that Zn would not diffuse from α brass into a single crystal of Cu about which it had been cast until the sample was mechanically deformed, is doubtless to be interpreted simply as evidence for an intervening oxide film formed during casting; her observation that Zn will diffuse from the vapor phase into a single crystal of Cu is evidence enough on the point, for there is no special circumstance attending the gaseous source of the diffusing element which makes the result anomalous. These results have been confirmed in my laboratory (Fig. 11). It is true that diffusion in single crystals is often extremely slow and may escape detection or measurement in comparison

* Rosenhain's²²³ suggestion that diffusion should be studied in single crystals prepared in different ways, i.e., by freezing and by strain-anneal, should be followed. Dehlinger⁶³ has observed that such crystals display different tensile yielding characteristics.

to the more rapid diffusion along a grain boundary and thus within an aggregate.

There can be no doubt, however, that diffusion is a structure-sensitive property. Fonda, Walker, and Young³⁵ showed that the rate of diffusion of Th in a Pintsch single crystal of W, as measured by the electron-emission method employed by Langmuir^{179,181}, is greatly increased by coiling the crystal even though there was no visible evidence of crystal fragmentation; upon annealing the distortion was relieved and the diffusion coefficient reverted to near the original value, again without detectable fragmentation. Earlier observations by Zwikker³⁰² showed that Pintsch single crystals of W, which are known to be less dense and thus less perfect than crystals grown from a vapor phase, display a diffusion coefficient for C from 10 to 30 times greater than for the more perfect crystals. For Pb, Seith and Keil²³⁹ could find no effect of cold-work, obviously owing to the low recrystallization and recovery temperature of lead; 0.3 per cent Au, however, was found to raise the recrystallization and recovery temperature to such an extent that the effect of distortion became evident in an increased rate of diffusion. Self-diffusion in Bi is markedly structure-sensitive in keeping with the semi-brittle nature of the element, as shown by Seith²³⁴. In order to get reasonably reproducible results it was found necessary to freeze the sample with great care and to anneal carefully; working increases the coefficient of self-diffusion, and annealing lowers it in the expected fashion.

The recent work of Finch, Quarrell and Roebuck^{83,273} on electron diffraction from metallic layers deposited on polished and on etched metallic surfaces is highly interesting in this connection. Although the exact nature of the polish layer is not yet certain, according to Germer⁹⁶, despite the conviction on the part of the English that the existence of a Beilby amorphous layer has been proved, the analysis of metallic layers obtained by deposition from the vapor does not seem involved in this dispute. It was observed that the electron diffraction spectrum of such layers when deposited on a polished surface disappears with extreme rapidity, though when the deposition is made on an etched (undistorted) surface of the same metal the spectrum is retained indefinitely. For example, a very thin layer of Zn deposited on a polished Cu disk was observed to begin to fade in one second, and could no longer be seen after 10 sec. Successively deposited layers disappeared more and more slowly until the twelfth layer could be seen after 4 hr. The Cu disk finally took a brasslike color, indicating the formation of a solid solution of Cu and Zn. A comparable experiment, made with one layer of Zn on an etched disk, showed the Zn spectrum to be still visible after $1\frac{1}{2}$ hr. Similar experiments on the deposition of Zn, Sn, Pb and Ag on polished and etched surfaces of mild steel, Pb, Au, Cu and Zn gave similar results, the time between deposition and disappearance varying from one combination to

another. These time periods seem to be in the order of the expected diffusion coefficients, though a complete comparison has not been made. The particular importance of this work is its demonstration that the rate of diffusion in distorted and cold-worked metals is far greater than in undistorted metals.* Since the experiments may be performed at room temperature, it is possible to study the effects of distortion without interference from simultaneous recovery and recrystallization. The method seems to be one of rather rare promise in the study of diffusion phenomena, and should be exploited to the fullest. Valuable qualitative information could be procured on such questions as the anisotropy of diffusion in noncubic metals, on the effect of grain size on the rates of diffusion without confusion from simultaneously changing grain size, and on the effect of third metals on the rate of diffusion; it seems possible that the method could be made at least semiquantitative.

It is, of course, to be expected that diffusion should be more rapid in distorted metals than in undistorted metals, for distortion produces a less dense structure in which the intensities of the interatomic forces should be less (the compressibility is greater, for instance) and produces also a less symmetrical force field (or charge density pattern), both effects contributing to a higher rate of diffusion. Ordinarily, however, it is difficult to demonstrate the effect, for as evident from the recent work by Mooradian and Norton²⁰, the rate of recovery from the effects of strain is much more rapid than the rate of measurable diffusion. Only when techniques of special sensitivity are applied, such as those employing thermionic emission, radioactivity or electron diffraction, or when the metal shows an unusual reluctance to recover or recrystallize, can the effect be demonstrated.

The solid solution formation which always accompanies diffusion (except in self-diffusion) creates two types of distortion: a microscopic distortion which is that characteristic of the solid solution state itself, evident in a broadening of X-ray diffraction lines, and a macroscopic distortion which is that brought about by gross volume changes accompanying the penetration of diffusing atoms into regions of low concentration with the resultant general readjustment of volume by flow, which of course involves distortion. This type of distortion may lead to some recrystallization and grain growth^{118,119,188}.

When Zn vapor diffuses into a bicrystal of Cu, the original sharply defined and nearly straight grain boundary may be replaced by an irregular boundary and new crystals, and occasionally twins may be formed, as shown in Fig. 14²⁰⁴. The absorption of Zn causes a volume increase and

* It is possible that etching produced films which would inhibit diffusion, and this possibility should be investigated—or a different technique developed which would avoid films—before such experiments are used to obtain evidence for rates of diffusion.

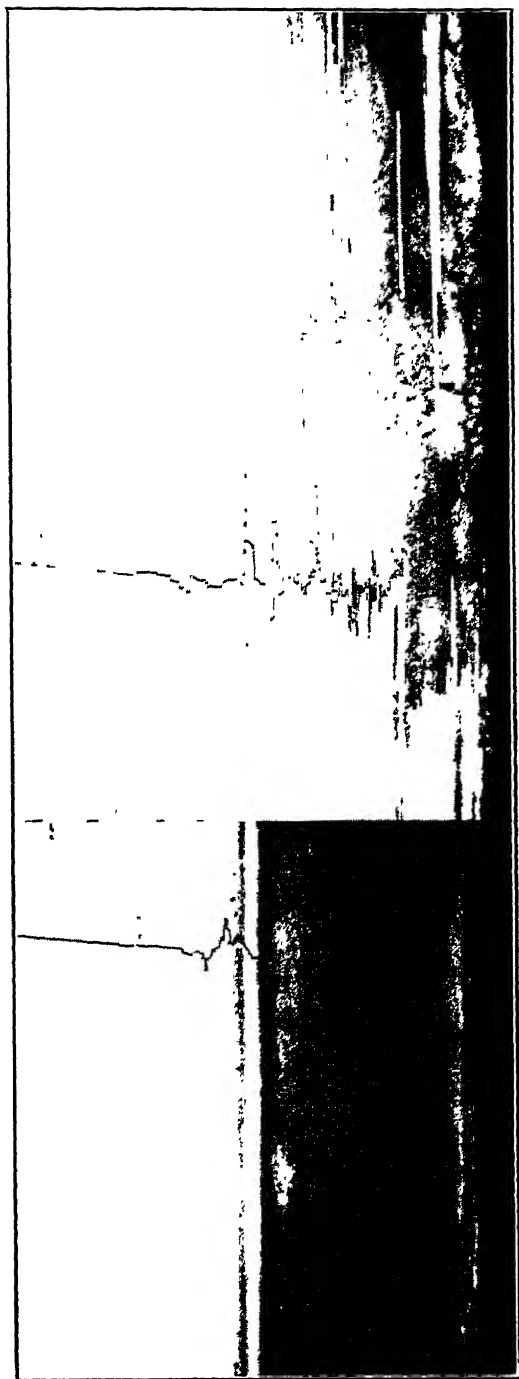


FIG. 14.—PENETRATION OF ZINC INTO BICRYSTAL OF COPPER²⁰⁴.

Left: Bicrystal of Cu packed in α -brass chips; held one week at 775°. Etching: Ammonia + hydrogen peroxide. $\times 100$. Showing α brass at bottom (stained), Cu at top, grain boundary running from top to bottom, and no preferential penetration along grain boundary.

Right: Same treatment as left side. Etching same as left, except that there was little staining. Showing recrystallization along grain boundary.

the inner constraint generates stresses which manifest themselves in recrystallization and in twin formation. It has been observed that twins are more profuse in annealed cast brass and bronze than in the unannealed casting; in this case local volume changes accompany atom transfer in the same way as in the grosser bicrystal. Generally, however, no great change in grain size accompanies homogenization in dendritically segregated castings, judging from the work of Mathewson¹⁹⁷, of Adcock²²⁴, and of Masing¹⁸⁸; diffusion at high temperatures favors some grain growth and at low temperatures grain refinement^{5,141,196}. More extensive studies are needed on this point.

GRAIN-BOUNDARY DIFFUSION

Grain boundaries, as usual, present an interesting case. Dushman and Koller¹⁸¹ demonstrated that the rate of diffusion of Th in W is dependent upon grain size, and Clausen⁵³ showed that diffusion in fine-grained W filaments at ordinary filament-operating temperatures is almost exclusively along grain boundaries. Van Liempt¹⁸⁴ observed that the rate of diffusion of Mo in W is ten times faster at 1600° in an aggregate of W crystals of 20 μ average grain diameter than in a single crystal. Langmuir¹⁸¹, and Fonda, Walker and Young⁸⁵ proved that a constant rate of diffusion of Th in W can be obtained for aggregates if all data are reduced to apply to the single grain—in order to cancel the effects of grain-boundary diffusion. These workers calculated the rate of diffusion of Th in W within a single crystal and along a grain boundary¹⁸¹:

$$\text{For volume diffusion: } D = 1.00 \cdot e^{-\frac{120,000}{RT}} \quad [16]$$

$$\text{For grain-boundary diffusion: } D = 0.74 \cdot e^{-\frac{90,000}{RT}} \quad [17]$$

Thus at 2400°K. the rate of diffusion is approximately 100 times greater along a grain boundary than within the grain.* The heat of diffusion, Q , is properly higher within the grain, for here the atoms are held in greater restraint and a greater energy of activation is required to set them free.† In many ways, as Langmuir¹⁸¹ and van Liempt¹⁸⁴ have pointed out, and as metallurgists have long assumed, the grain boundary is quite similar to regions of distortion within a crystal, and in this light

* It has been suggested¹⁸⁴ that grain-boundary diffusion is less likely to obey a precise law than intragranular diffusion, owing to varying orientation relationships of the opposite grains. There are no experimental data as yet on this interesting point; its discovery would imply an anisotropy in grain-boundary diffusion which seems unlikely in cubic crystals.

† The inference that the work of Fonda et al. implies that grain size affects the constant A alone, and not Q , is of course incorrect.

the higher diffusion coefficient is to be expected.* Zwikker³⁰² found that the diffusion of C in W is four times as rapid in fine-grained W as in single crystals. G. Edmunds⁷⁷, of the New Jersey Zinc Co., reports that the diffusion of Cu into single crystals of Zn cannot be observed, though the process occurs rapidly in polycrystalline Zn; recent experiments by F. N. Rhines³⁰⁴ have demonstrated that diffusion of Cu into

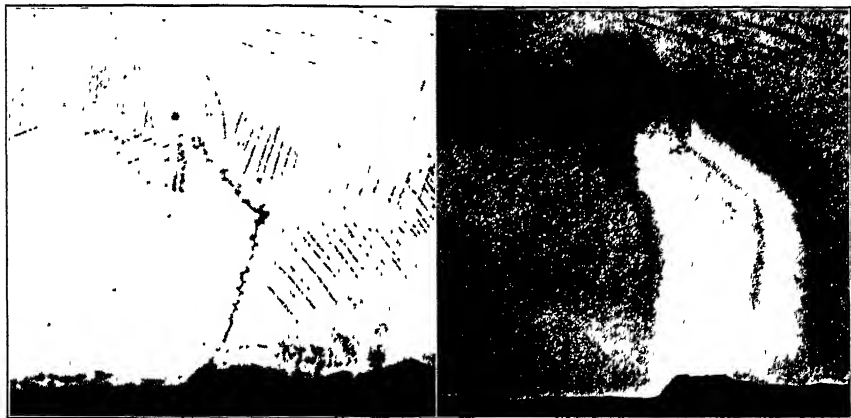


FIG. 15.—LOSS OF ZINC FROM α -BRASS BICRYSTAL²⁰⁴.

Left: Bicrystal of α brass (70:30) held one hour at 790° in vacuum. Etching: Ammonia + hydrogen peroxide. $\times 100$; reduced $\frac{1}{8}$ in reproduction. Showing crack along grain boundary.

Right: Same treatment as left, but stained by etching. Showing loss of Zn around crack (Cu-rich portion less stained).

single crystals of Zn may readily be effected, though the rate of diffusion of Cu into polycrystalline Zn is approximately six times as rapid. When Zn is withdrawn from a bicrystal of α brass, it leaves the boundary more rapidly than the grain as shown in Fig. 15; this may be the result of more rapid diffusion at the grain boundary, but since a shrinkage in volume accompanies the loss in Zn, the crystal tends to open or cleave at the

* The work of Dushman and of Langmuir has been seriously questioned by Geiss and van Liempt^{92,94}, who adduced data on the temperature coefficient of resistance of W containing Th and concluded that Th is not in solid solution in W but lodged at the grain boundaries, and by Gehrts⁹¹, who attempted to explain the thermionic behavior of thoriated filaments on the basis of grain-boundary diffusion alone. Dushman and Fonda⁷⁴ report, however, that wires made from mixtures of W and Th when heated in nonoxidizing atmospheres exhibited values for electrical conductivity and temperature coefficient appreciably higher than those for pure W; similar results were obtained for thoriated Pintsch wires when heated in reducing conditions with partial reduction of thorium to Th and the solution of Th in the solid W. In view of this, the analytical methods used by Langmuir and Dushman to determine diffusion coefficients seem beyond dispute. Recent observations by Becker¹⁷ using the electron microscope indicate that Th atoms reach the surface of W in spurts rather than at a uniform or gradually changing rate as implied in a diffusion equation; no satisfactory explanation of this effect is as yet available (cf. ref. 37).

grain boundary, thus exposing the boundary surface forming a crack, and the effect may be only this, particularly in view of the results shortly to be mentioned on the diffusion of Zn into a bicrystal of Cu.* E. H. Dix⁶⁹, of the Aluminum Company of America, states that diffusion in Al alloys is often observed to follow grain boundaries, as shown in Fig. 16, which illustrates the diffusion of Cu from duralumin into the pure Al coating in Alclad duralumin; the preferential penetration along grain boundaries is shown by the staining effect. Similar results have been

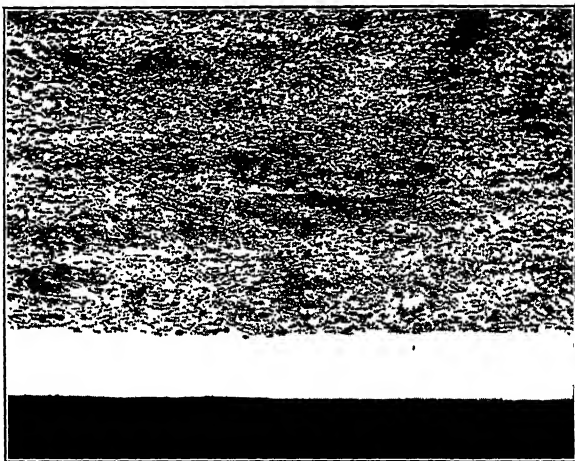


FIG. 16.—PENETRATION OF COPPER FROM DURALUMIN INTO ALUMINUM COATING⁶⁹.

Commercial heat-treatment of Alclad duralumin. Etching: 1 per cent HF in water. $\times 100$; reduced $\frac{1}{4}$ in reproduction. Showing preferential penetration of Cu along grain boundaries in pure Al coating.†

given by N. B. Pilling²¹⁵ for the diffusion of Cr from a Cr-Ni alloy into Ni; it has recently been reported that Cu penetrates along the grain boundaries of γ Fe in annealing bimetal strip²²⁹. In all the examples cited, then, diffusion at the grain boundary is more rapid than within the grain.†

On the other hand, Seith and Keil²³⁹ were unable to detect any effect of grain size upon the rate of self-diffusion in lead. Elam⁷⁹ reported that Zn does not penetrate preferentially along the grain boundaries of Cu and this has been confirmed by F. N. Rhines²⁰⁴, as shown in Fig. 14.‡ Fig. 12, illustrating the diffusion of C in γ Fe, likewise shows no prefer-

* Desch⁶⁶ states that Zn is lost on vaporization from α brass more rapidly from twin boundaries than from within the grain.

† The electrical conductivity and self-diffusion in CaCO_3 and NaNO_3 have been observed to increase as the grain size decreases; i.e., the rate of diffusion is greater at the grain boundary than within the grain¹³⁴.

‡ Yamauchi²⁹⁹ observed the contrary, for some unknown reason.

ential penetration of C along the γ Fe grain boundaries,* as does also Fig. 13, illustrating the penetration of N into α Fe.† This lack of preferential penetration of N along the grain boundaries of α Fe is apparently confirmed by recent observations by C. Wells²⁰⁴ on the effect of grain size on the depth of nitrogen penetration as judged by the appearance of nitride "needles." A sample of hydrogen-purified Armco iron in rod form, $\frac{1}{8}$ in. diameter, with 200 grains per sq. mm. and another of the same external dimensions with one grain per sq. mm. were nitrified in ammonia at 525°C. for 24 hr.; in each nitride "needles" were visible to a depth of 1 mm. \pm 0.05 mm., from which we may conclude that any effect of grain size was restricted to less than 10 per cent. In these cases, then, there is no effect of grain size upon the rate of diffusion, no increased diffusion along the grain boundary. We have no information whatsoever upon the factors which determine whether the rate of diffusion at a grain boundary should be faster or slower than within the grain.

When diffusion along a grain boundary is more rapid than within the grain, the diffusion coefficient measured in an aggregate in the usual way is some average of intragranular and intergranular diffusion, a mixed coefficient, as pointed out by van Liempt¹⁸⁴, rather than a unique constant. As we consider the many reported measurements of diffusion coefficients where, apart from the exceptions noted above, no attention whatsoever was paid to the effect of grain size, we may well be concerned as to the real meaning of these coefficients; if, in these cases, grain size is a factor, the published values refer to some often unknown or unstated grain size, and even perhaps to a changing grain size. Obviously more care should be employed in such measurements, with a more general use of the metallographic microscope. It may be said that the ideal diffusion is that subsisting between two single crystals, for only in this case is the uncertain effect of grain boundaries absent; van Liempt¹⁸⁴ alone has made such a measurement, though the work on the diffusion of gaseous metals into single crystals seems equally satisfactory.

SURFACE DIFFUSION

It was shown by Volmer²⁵⁵⁻²⁵⁹ and his coworkers that Hg atoms condensing upon Hg crystals do not remain at the point of impact, but retain

* Rowland and Upthegrove²²⁶ recently showed that commercial steels of different "inherent" austenite grain size decarburize between the A_1 and A_3 temperatures in "wet" hydrogen at different rates and very surprisingly found that the steels of the larger grain size decarburized the more rapidly; this is probably not valid evidence for the effect of grain size on diffusion, for, as these authors suggest, the steels of smaller grain size doubtless contained greater quantities of SiO_2 and Al_2O_3 which might well impede diffusion.

† These results seem satisfactory enough, though the point would be more adequately proved by a careful determination of the effect of grain size upon the rate of diffusion performed in the orthodox fashion of the chemical analysis of layers.

a mobility permitting them to migrate along the surface of the crystal, a sort of surface self-diffusion. This suggests that similar migrations may occur with foreign atoms, and such migrations have been noted in a number of cases. The three types of diffusion are shown diagrammatically in Fig. 17, which has been drawn to illustrate anisotropy also.*

The study of activated thermionic filament has given a great deal of information on true surface diffusion. The surface films of several elements of W obey the diffusion laws and possess temperature coefficients of rates of diffusion quite analogous to those for volume diffusion; the

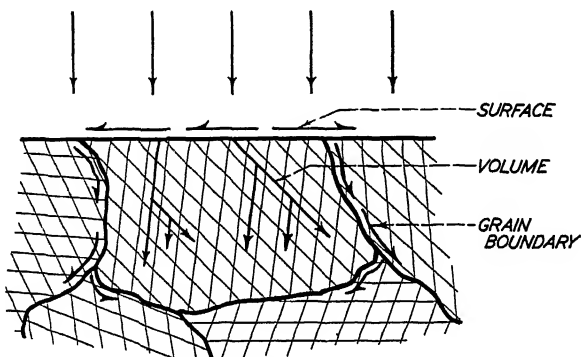


FIG. 17.—TYPES OF DIFFUSION IN CRYSTAL AGGREGATE.

process may be conceived as a two-dimensional diffusion. Taylor and Langmuir^{270, 271} demonstrated that Cs is mobile on W and found a Q value of 14,000 cal. for a monatomic layer; when a second layer is added, the rate of diffusion is ten thousand times faster at 500° K., and the Q value is only 2500 cal., quite in keeping with the fact that the Cs atoms are moving in a much less intense force field when moving upon a Cs film than when moving on a W surface. It was found that the diffusion coefficient varies with concentration as in solid alloys. Becker¹⁶ likewise studied films of Cs on W and also of Ba on W; in a fascinating experiment

* Surface mobility appears in many systems, and in many cases the phenomenon can more properly be described as a spreading rather than a diffusion. For instance²⁴⁸, it is known that ThB is mobile on quartz and that a layer of benzophenone is mobile on surfaces of glass, mica, and diamond, and its rate of spreading is characterized by a large temperature coefficient in the case of diamond; the spreading of Hg drops on metal surfaces is a somewhat similar case^{4, 95, 254}, and in this instance the preferred orientations generated in the cold-rolling of foil are reflected in the formation of ellipses of spreading. In these cases, however—and in others like them—the process involved is one of spreading in a liquid or in a liquid-solid system than of diffusion in a solid system.

Lukirsky¹⁸⁶ showed that Th adsorbed on one side of a filament will move around to the other side. Bosworth²¹ studied Na on W and found evidence of grain fragmentation accompanying the diffusion of Na, a rather remarkable fact. The work of Langmuir and his collaborators, particularly for Th on W^{32,181,271}, which is of particular interest because of the completeness of the data on volume and grain-boundary diffusion in this system. Th diffuses out of the single W grain and reaches the grain boundary, at which point its movement accelerates one hundred times, finally arriving at the surface. At this point it either evaporates, or if the temperature is low enough, it diffuses along the surface at a rate increased tenfold, forming a monatomic layer with one Th atom for each two underlying W atoms. This rapid rate is again characterized by a smaller Q value, for here again the atoms move with less restraint from the force field. We have then^{180,181} for Th on W:

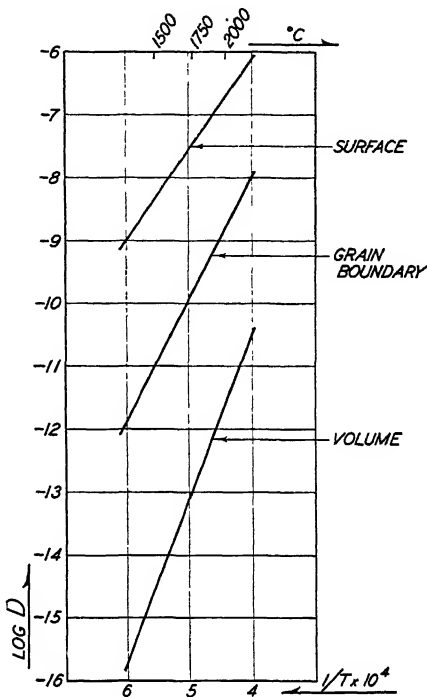


FIG. 18.—DIFFUSION OF THORIUM IN TUNGSTEN¹⁸¹.

$$\text{For surface diffusion: } D = 0.47 \cdot e^{-\frac{66,400}{RT}} \quad [18]$$

The relationships among the three types of diffusion of Th and W are shown graphically in Fig. 18, plotted from the three equations given above, which shows an increasing rate of diffusion in the sequence volume-boundary-surface, and shows also decreasing slopes, or decreasing Q values in the same sequence. This is the most complete picture now available for diffusion in any system whatsoever and may well be considered as a classic piece of work in this field.

Schwartz²³¹ states that Po is mobile on the surface of Ag, but not noticeably into the interior²⁰⁵; it is quite possible that the difference may be one only of rate, for we have seen that in the case of Th on W surface diffusion is much faster than grain-boundary or volume diffusion. It is to be presumed that surface mobilities may occur when volume diffusions are really absent, but there is no information available on this point

except that just cited.* It would be very interesting to have data on surface diffusion for more familiar metal systems, but methods of measurement in general are lacking; thus far the data are nearly exclusively from the field of thermionics.

METALLURGICAL PROCESSES

It will be evident to the metallurgist from the above that diffusion plays a very important part in many metallurgical processes. The subject has been too little developed and most metallurgical processes are too complicated to permit analysis of particular problems from the point of view of diffusion, but the opportunities are so many and so promising that some of the problems should be stated if not solved.†

Carburization is a process which, while requiring diffusion for its accomplishment, offers special complexities.‡ Although Bramley's work²³⁻³¹ is not entirely satisfactory, it does afford a great amount of information. Bramley derived diffusion coefficients from both carburization and decarburization experiments with identical results when carburization was performed by the use of CO and hydrocarbon gases and when decarburization was performed in "wet" H; when, however, mixtures of CO and CO₂ and when wet N were used, different diffusion curves were obtained; it appears, then, that the rate of reaction at the surface may in some cases be the controlling rate, rather than the rate of diffusion as generally assumed. As carried out practically, not only are Fe and C involved in carburization and decarburization but also many other elements, particularly O and N (and sometimes H) in the carburizing gases, and O, N, P, and alloy elements in the solid steel. In addition, the chemical identity of the compounds obtaining in the gas phase at the gas-metal interface and those formed at the interface by reaction with the metal have not definitely been identified. A physicochemical analysis of the carburizing (and the nitriding) processes is much needed, for many peculiar effects have been noted^{115,139}; from the standpoint of physical

* There may be some relationship between the tendency to form oriented overgrowths and surface diffusion, as though a matching of atom planes at an overgrowth interface were a sort of two-dimensional solid solubility analogous to the requirement for solid solutions for volume diffusion. Oriented overgrowths have been observed between lattices which show no solid solution formation, or extremely little, such as NaCl on galena²⁰¹.

† The manufacture of bimetal strip and the surface improvement of metals by diffusion have led to many investigations which may be merely noted here^{48-51, 56-62, 98, 111, 114, 117, 163-166, 175-178, 185, 208, 300}. The rate of oxidation of metals is determined by the rate of diffusion of O through the oxide layers, but this is not directly related by the present subject²³².

‡ Work on this subject has, of course, been voluminous, but little of it adds much information on diffusion^{1, 5, 43-46, 112, 142, 227, 228, 275}.

chemistry, the field is almost untouched. Such an analysis must consider the nature and the rates of surface reactions and the effects of accessory elements present initially in the steel and added during the process. The uncertainty in the present theories of decarburization is apparent from the discussion in the recent paper by Rowland and Upthegrove²²⁶. Houdremont and Schrader¹⁴⁰ recently studied the rates of carburization of a number of alloy steels and concluded that Cr, Mo, and W decrease the rate of diffusion of C, while Al and Si are of uncertain influence and Ni, Co, and Cu increase it; these conclusions are drawn from penetration curves and from chemical analysis of the surface—the experiments were not designed to give true diffusion coefficients and the conclusions seem unwarranted. The work of Baukloh and Guthman¹⁵ on the decarburization of alloy steels is similarly of little direct use as evidence for diffusion. Tammann's²⁶² study of the rate of carburization of alloys of Fe seems too qualitative to be really useful, though his attack should be continued with a more careful analysis of carburizing conditions and of rates of diffusion; properly carried out, such experiments would add much valuable information to the subject of carburizing and also that of reactions in steel, as evident from the discussion below.

The homogenization of alloys obviously requires diffusion, and the rates of homogenization, at least in pure binary systems, should be easily explained on the basis of rates of diffusion of the metals involved; indeed Weiss²⁹⁵, following the suggestion of Tammann²⁶¹, found that the rates of homogenization in segregated castings of Ag-Sb alloys with 14 per cent Sb containing primary Ag_3Sb varied exponentially with temperature and thus proposed an exponential law for diffusion rates. Thus times for "equivalent homogenization" at different temperatures can be predicted from a single experiment and the application of equation 11 rather than determined by exhaustive test. In ternary alloys the case is more difficult because of widely varying diffusion rates of the component metals, but it is evident that the more slowly diffusing element will be the controlling rate, as in segregated Fe-Mn-C alloys, in which the rate of solution of the Mn-bearing Fe_3C is much slower than that of Fe_3C in simple carbon steels, owing evidently to the low rate of diffusion of Mn, or as in ordinary steels where the persistence of P-segregation is so familiar. These cases are complicated, however, and have not been carefully studied.

Dushman⁷³ in 1929 pointed out that many metallurgical processes, such as hardening by cold-work and general alloy reactivity, should depend upon the energy states of the atom and should—and indeed appear to—follow exponential laws similar to that given for diffusion in equation 11. Upon the statement of the theory of age-hardening by Merica, Waltenberg and Scott²⁰³, it became clear immediately that diffusion obtained in the age-hardening process^{148, 202}, but quantitative

analyses of its role were lacking until recently. Seltz and Hone¹³⁸ in 1933 showed that the initial rates of precipitation of the γ -phase from the terminal solid solution of Ag in Al (as measured by changes in electrical resistance) varied exponentially with temperature and could be expressed by an equation of the type of 11. The aging curves for an alloy with 38 per cent Ag are shown in Fig. 19, and the plot of the logarithm of the initial rate against the reciprocal of the aging temperature (compare Fig. 5) is given in Fig. 20. The Q value derived from this plot

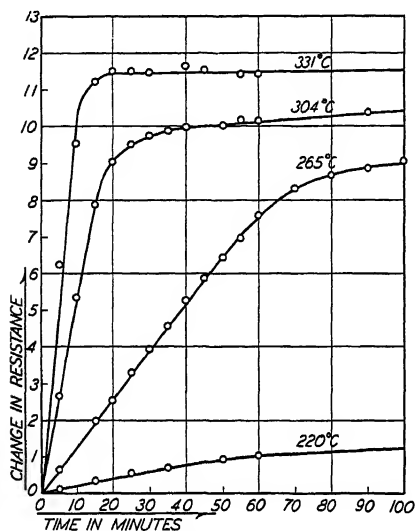


FIG. 19.—CHANGE IN ELECTRICAL RESISTANCE ON AGING AN ALUMINUM-SILVER ALLOY WITH 38 WEIGHT PER CENT SILVER¹³⁸.

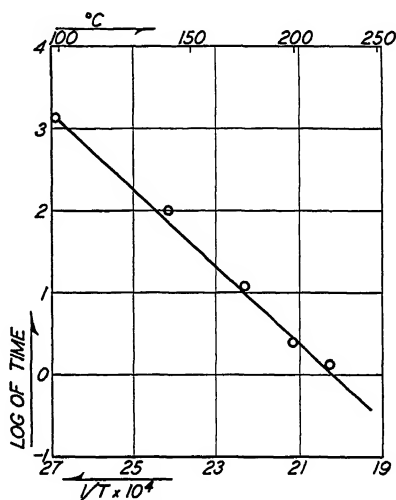


FIG. 20.—INITIAL RATES OF AGING AT DIFFERENT TEMPERATURES OF AN ALUMINUM-SILVER ALLOY WITH 38 WEIGHT PER CENT SILVER¹³⁸.

is of the order of 22,000 cal., a value not unreasonable for the system concerned. This is strongly suggestive that the rate of diffusion is the controlling factor in determining the rate of aging, but the argument would be more convincing if it could be shown that the Q value found is identical with that derived from direct measurements of rates of diffusion, and this test is now underway.

Last year Jenkins and Bucknall¹⁴⁹ showed that the times necessary to bring an aging alloy to its maximum hardness or strength could be plotted in logarithmic form against the reciprocal of the temperature of aging to give a straight line, as shown in Fig. 21, thus associating the rate of aging with the rate of diffusion. Here again a comparison of the derived Q values with those determined from measurements on the rate of diffusion are desirable; the Q values derived from their graphs all seem too low. Bucknall⁴⁰ later extrapolated the curve for duralumin to room

temperature and calculated that duralumin will not overage at this temperature in one million years!

It is obviously of great importance to attempt an exact correlation between the rates of aging and rates of diffusion, for with this established information in one field would reinforce information in the other; perhaps a planned program of search for age-hardening systems of predictable behavior might be developed. In a qualitative way this appears promising, for systems composed of high-melting metals, like Fe-Mo, Fe-W²⁵⁹ and Cu-Be, in which diffusion coefficients should be high only at high temperatures, require high temperatures to give appreciable rates of aging, whereas systems composed of low-melting metals, like duralumin, age appreciably at room temperatures. We may note also that the rates of age-hardening in alloys of α Fe with C and N, as pointed

out by Bain and Davenport¹², are in the order of their respective diffusion coefficients in γ Fe and therefore presumably also in α Fe, and perhaps we might suspect that overstrain aging in α Fe, which we now firmly believe to be caused by O is also a process of precipitation, requiring distortion—overstrain—to accelerate the rate of precipitation to appreciable values owing to the low rate of diffusion of O in α Fe.*

Evidently, however, we must proceed with much caution. If we plot Köster's¹⁷² data on the rate of aging of alloys of α Fe with C in the manner shown in Fig. 21, we obtain a Q value of 5000 cal. Now, Bailey and Roberts¹⁰ have plotted the times for complete spheroidization of pearlite in this way and have concluded that the linearity of the plot proves spheroidization to be a simple process of agglomeration governed by rates of diffusion^{297,298}; however, the Q value derived from the plot of Bailey's data is 28,000 cal., a value five times that derived from Köster's data on aging, a discrepancy far too serious to be overlooked. Whether we can compare such diversified data on a single basis may well be questioned—how can we directly compare hardness data and electrical conductivity data, how can we assume that equal degrees of change in these properties mean equal degrees of precipitation? There is probably little use to discuss less certain details of the age-hardening process²⁵²; it might,

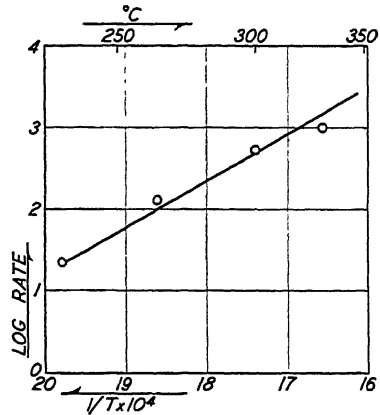


FIG. 21.—RATES OF AGING AT DIFFERENT TEMPERATURES FOR THE ALLOY LAUTAL AS MEASURED BY THE TIMES TO ATTAIN MAXIMUM TENSILE STRENGTH¹⁴⁹.

* Here again we may assume that the rate of diffusion of O in α Fe is less than that of C or N since the rate of diffusion of O in γ Fe is less.

however, be suggested that the preferential precipitation of an aging constituent at the grain boundaries may be associated with an increased rate of diffusion at the grain boundary, and that this effect may be lacking in systems in which grain-boundary diffusion is no more rapid than intragranular diffusion. Superficially this thought seems attractive, though we must admit one uncertainty—the grain boundary by reason of its characteristic distortion directly encourages nuclei formation, and though nuclei formation requires diffusion we cannot conclude that the number of nuclei is proportional to the rate of diffusion.

The aging of ternary alloys is accompanied by complicated diffusion effects. If a compound is to precipitate from a solvent, such as Mg_2Si from Al, it is evident either that the two atoms must diffuse at the proper relative rates to give the compound whatever the normal rate of diffusion of each may be, as Mrs. Freche⁸⁷ suggests, or that the rate of diffusion of the more slowly diffusing metal controls the rate of precipitation; it is also at least possible in such cases that some phase other than the predicted compound may appear first on precipitation, as shown by Mehl Barrett and Rhines¹⁹⁹ for the system Al- Mg_2Si . It might be noted here that experiments such as these offer the opportunity to demonstrate the presence or absence of molecules in solid solution, for though this point has never seemed real, it does nevertheless frequently appear in metallurgical writing; the diffusion into pure Cu of the "compound" Ni_2Si in solid solution in Cu may furnish the desired direct evidence, for if the entity Ni_2Si actually exists in solid solution, it must diffuse as such and penetration curves will disclose this.

We may note here that the effect of cold-work in accelerating the rate of aging may be merely one of the acceleration of diffusion by lattice distortion, yet again we cannot disregard the effect of increased nucleation.

In transformations of the austenite-pearlite type there is even less certainty, though an understanding of the mechanism of these reactions is of fundamental importance in the science of the heat-treatment of steels.* These processes differ from age-hardening processes in the occurrence of an allotropic change in the solvent phase; this change causes the rate of transformation at first to increase on lowering temperature and then to decrease as shown in the work of Bain¹¹. This is doubtless the result of the cooperation of two processes, as suggested by Austin⁹, one of which—the one with rate decreasing with temperature decrease—may well be the diffusion of C in austenite during its segregation as Fe carbide, as I pointed out in the discussion of Austin's paper while the other—the one with rate increasing with temperature decrease—

* The reactivity of solid mixed inorganic compounds has received much attention and it has been shown that diffusion rates exercise a controlling effect^{120-123, 280, 285}. The rate of formation of superstructures is likewise conditioned by diffusional rates^{22, 290, 292, 293}.

may be a rate determined simply by the free energy change, even though the orthodox thermodynamicist may insist on the absence of any formal correlation between free energy change and rate of reaction. It is, of course, obvious that the formation of pearlite requires diffusion;* the formation of martensite, however, requires no diffusion, for the distribution of C in the initial "white" stage of martensite is the same as in austenite; i.e., it is statistically uniform.

The effect of alloying elements on retarding the rate of austenite decomposition is doubtless associated with decreased rates of diffusion, though the matter is by no means clear. Recent experiments in my laboratory on the rate of decarburization of Hadfield's Mn steel and of a simple C tool steel of the same C content disclosed identical rates for the two steels, so that we may hardly ascribe the retarding effect of Mn on the rate of decomposition of austenite to a retarding effect upon the rate of diffusion of C in austenite, and we are more inclined to explain the retardation by the necessity for the simultaneous diffusion of Mn required by the formation of Mn-bearing carbide²⁹⁶ and the slow rate of diffusion of Mn in austenite as compared to C^{213, 296}. Ni, however, likewise retards the decomposition of austenite, yet it does not seem to form a carbide in steels, so that our first explanation hardly holds here. In Mn-steels, the carbide contains Mn much in excess of the austenite, and thus the Mn must diffuse in quantity to a relatively thin layer of carbide in pearlite, while in Ni-steels the carbide contains little or no Ni and the Ni must diffuse out of the relatively small regions to be occupied by the carbide into the relatively thick layers of ferrite. These phenomena, from the point of view of diffusion rates, are obviously complicated, but properly conducted determinations of diffusion coefficients in alloy steels should nevertheless lead to a basic science of the factors which control the rates of decomposition of austenite.

CONCLUSION

It must be clear from the above that much experimental work remains to be done upon the subject of diffusion in solid metals, both for the purpose of determining diffusion coefficients, which is a relatively simple matter, and for the purpose of explaining alloy behavior, which like so much in metallurgy in many cases can be extremely complex. The pursuit of such important subjects in the science of metals should commend itself to every metallurgist, for the development of the science of

* The effect of decreasing grain size on increasing the rate of decomposition of austenite can hardly be ascribed to an increasing rate of diffusion at the grain boundary, for as shown earlier in this paper the rate of diffusion of C at the γ Fe grain boundary seems to be no more rapid than within the γ Fe grain. In agreement with most writers on this subject we must assume that the effect of the grain boundary is chiefly one of nucleation.

metals is of great importance. Metallurgy is in that happy state where there is much in the future, where simple facts and simple theories remain to be discovered, and where the development of the science will lead to practical application of wide industrial and social consequences.

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Properties and Alloys of Beryllium

By LOUIS L. STOTT*

(New York Meeting, February, 1936)

It is well known that the oxide of beryllium was identified as a new "earth" in 1797^{1†} and the metal first isolated in 1827². The history of the many difficulties encountered by early investigators, the laboratory achievements of Lebeau³, Fichter⁴ and Oesterheld⁵, and the eventual development of methods for commercial production are well covered in the literature, particularly in the authoritative published work of Siemens and Halske⁶ reviewing their comprehensive investigation of the element. Accordingly it has seemed desirable to restrict this paper to the properties and uses of beryllium and its alloys.

PROPERTIES OF BERYLLIUM

A comprehensive summary of the available data on the properties of beryllium is given in "Gmelius Handbuch der Anorganischen Chemie⁷." The metal is steel gray in color. A fractured surface exhibits a bright luster, which does not appear to change with long exposure to air, probably because of a thin, transparent protective oxide coating. The specific gravity is approximately 1.8. Although there is no recorded actual determination of Young's modulus of elasticity, it has been estimated⁸, according to Fessenden's law, to be 30,000 kg. per sq. mm., or about 30 per cent higher than steel. Beryllium appears to have an electrical conductivity approximately $\frac{1}{12}$ that of copper. The physical constants as available in the literature are given in Table 1.

One of the outstanding properties of beryllium is its great affinity for oxygen, nitrogen, sulfur and carbon. One gram of beryllium takes up 1.774 grams of oxygen and will liberate approximately 15.23 kilogram-calories in the combination. The metal apparently reacts with all known oxides at high temperatures; in fact, beryllium will alloy with thorium and zirconium if melted in crucibles of their oxides.

The true physical properties of beryllium are still somewhat in doubt, since very small amounts of impurities appear to cause a large variation

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† References are at the end of the paper.

in hardness. Determinations running from 120 to 140 Brinell have been made on the 99.8 to 99.9 per cent metal⁹. Kroll¹⁰ reports 111 Brinell on several grams of approximately 99.95 per cent sublimed in vacuum. H. A. Sloman¹¹ has given a value of 60 Brinell for 99.99 per cent metal and suggests that a beryllium-beryllium oxide eutectic occurring at the grain boundaries is the troublemaker.

TABLE 1.—*Physical Constants of Beryllium*⁷

Atomic number.	4	Melting point.....	1285° C.
Valence.....	2	Specific gravity.....	1.85 at 20° C.
Atomic weight	9.02	Atomic volume.....	4.94 to 5.30
Linear coefficient of expansion.		20° — 100°	12.3×10^{-6}
		— 200°	13.3×10^{-6}
		— 300°	14.0×10^{-6}
		— 400°	14.8×10^{-6}
		— 500°	15.5×10^{-6}
		— 600°	16.1×10^{-6}
		— 700°	16.8×10^{-6}
Heat conductivity.....		$K = 0.3847 + 0.000751t$	
		— 0 000000468t ²	
		— 0 00000027t ³	
Young's modulus of elasticity.....		30,000 kg. per sq. mm. (calculated)	
Heat of fusion.....		345.5 cal. per gram	
Type of crystal lattice.		hexagonal close pack	
Axial ratio.....	1:1.58		
	$a = 2.283 \text{ \AA.}$	$c = 3.61 \text{ \AA.}$	
Hardness.....		120 — 30 Brinell (99.8 — 99.9 per cent)	
		111 Brinell (99.95 per cent)	
		60 — 65 Brinell (99.99 per cent)	
Vapor pressure.....		0.001 mm. Hg at approximately 1400° C.	
		5 mm. Hg at approximately 1530° C.	
		760 mm. Hg at approximately 3040° C.	
Electrical conductivity, reciprocal ohms.....		5.41×10^4 (20° C.)	

Chill-cast specimens of 99.8 to 99.9 per cent beryllium melted as carefully as possible are undoubtedly brittle at room temperature. The work of Sloman appears to indicate, however, that there is a certain amount of ductility if the metal is sufficiently pure. It must be admitted that often individual flakes obtained from chloride electrolysis appear somewhat malleable. However, the ductile beryllium prepared by Sloman at the National Physical Institute was apparently in very minute quantities and other investigators so far have not been able to duplicate his work.

Pure distilled beryllium has recently been hot-rolled in the laboratory down to sheets 0.020 in. thick. When hot it could be bent somewhat, but at ordinary temperatures the elongation appears very low. The hot-rollability was poor and could not be done without considerable cracking on the edges.

Up to the present time there have been very few applications for pure beryllium. In Europe some metal has been used for windows in X-ray tubes because of the transparency of the element to X-rays—nearly 20 times that of aluminum¹². The low tendency of the metal to sputter in cathode-ray tubes¹³ and its high reflectivity for ultraviolet light¹⁴ are of possible commercial interest. Of particular scientific interest is the work under Dr. Ernest Lawrence at the University of California on the manufacture of artificial radioactive substances through the use of neutron rays obtained by the bombardment of beryllium with high-speed protons and deutons¹⁵.

ALLOYS WITH LIGHT METALS

Having a place in the periodic system at the top of the second group, there has been considerable hope that beryllium might be somewhat similar to magnesium or aluminum in properties, or at least be a useful addition to light metals. The pure metal appears, however, to be too brittle ever to use structurally. Moreover, it seems that in most instances, rather than offering any marked new advantages, small additions of beryllium to aluminum alloys are either inert or similar to silicon in their alloying effects. Archer and Fink¹⁶, and later Matignon and Calvert¹⁷, have pointed out that pure aluminum could be age-hardened with beryllium. Unfortunately this tendency appears to be found only to a small extent in alloys of the duralumin type.

The Beryllium Corporation has investigated a wide series of beryllium-aluminum alloys containing more than 50 per cent beryllium. Although some of these compositions can be cold-rolled to unusually high tensile strengths, in comparison with other light alloys, their low ductility and very high cost has prevented commercial consideration.

There is some indication that small additions of beryllium may be useful in aluminum casting alloys. Masing and Koch¹⁸ have reported that in this way the resistance to wear of piston alloys can be considerably increased.

Magnesium and beryllium do not appear to form an alloy. However, the wide difference in melting points of the two metals makes research on the problem difficult and further investigation is being carried on in this field.

ALLOYS WITH NONFERROUS METALS

1. *Beryllium Copper*

The remarkable heat-treatable characteristics of beryllium-copper alloys were first discovered by Dr. G. Masing and his associates at

Siemens Halske in 1926¹⁹. Broad patent protection was obtained covering the heat-treatment of these alloys as well as certain applications²⁰.

Oesterheld, in his early work with beryllium, conducted an investigation of the system beryllium-copper and published the equilibrium diagram in 1916, but the quantities of metal at his disposal were unfortunately too small to determine any physical properties.

In the latter part of 1925, before becoming aware of the heat-treatable nature of the alloys, the Beryllium Corporation of America contacted the Anaconda Copper Co. and pointed out the hardening effect of beryllium on copper. As a result, the late W. H. Bassett, of the American Brass Co., conducted in 1926 an investigation of the behavior under mill conditions of copper when alloyed with beryllium²¹. In 1930, J. Kent Smith, of the Beryllium Corporation, checked the work of Siemens and Halske²², and shortly thereafter the American Brass Co. was asked again to consider the commercial application of these alloys with the added feature of heat-treatment.

Largely owing to the vision and efforts of Mr. Bassett, the American Brass Co. was the first organization in the United States to put on the market wrought beryllium copper. A few months later the Riverside Metal Co. also became interested in the sale of this alloy. These two companies have made noteworthy progress in developing markets for beryllium copper.

The principal industrial interest has been in the alloys containing from 1.5 to 2.75 per cent beryllium. The standard alloy rolled by several fabricators has contained approximately 2.25 per cent beryllium, balance mainly copper. In one alloy, 0.25 to 0.5 per cent nickel is added to restrict grain size during annealing. As is well known, copper alloys of the alpha solid solution type are sensitive to grain growth. This tendency in binary copper beryllium can be strongly restricted if the alloy is annealed and quenched from a temperature enabling a small amount of the beryllium to be present in the beta phase, or if sufficient beryllium is added to maintain some beta at the maximum quenching temperature.

The original work of Siemens Halske included not only binary beryllium copper but also ternary beryllium-copper alloys containing additions of a metal of the iron group or aluminum, manganese, magnesium, phosphorus, tin or zinc. In the United States, M. G. Corson, believing that Ni_2Be would have the same effect in copper as Ni_2Si , investigated the heat-treatable nature of beryllium-nickel-copper alloys²³. A thorough study of the physical properties of this ternary combination in wide ranges of composition was made by Masing and Poche²⁴. Recent investigation has given additional evidence that there are interesting ternary and quaternary combinations, which enable effective hardening with considerably less beryllium content.

The properties obtainable in sand castings of beryllium-cobalt-copper alloys are particularly outstanding. For example, an alloy containing 0.4 per cent beryllium, 2.6 per cent cobalt, balance copper, can be sand-cast and heat-treated to an average tensile strength of 95,000 lb. per sq. in. with an electrical conductivity of better than 45 per cent of copper. Other properties in the sand-cast state are given in Table 2.

TABLE 2.—*Physical Properties of Sand-cast Alloy Containing 0.4 Per Cent Beryllium, 2.6 Per Cent Cobalt, Balance Copper, after Heat-treatment*

STANDARD A.S.T.M. 0.505-IN. TEST BARS

Ultimate tensile strength, lb. per sq. in.	95,000
Elastic limit, lb. per sq. in.	85,000
Elongation, per cent in 2 in.	7
Hardness, Rockwell B, 100-kg. load.	97
Electrical conductivity.	45 to 50 per cent of copper

Wire of this alloy has been drawn to a tensile strength of 137,000 lb. per sq. in. and can attain a conductivity over 50 per cent of copper, as shown in Fig. 1. Although the tensile properties and hardness of this material do not approach those of the binary beryllium-copper alloys of

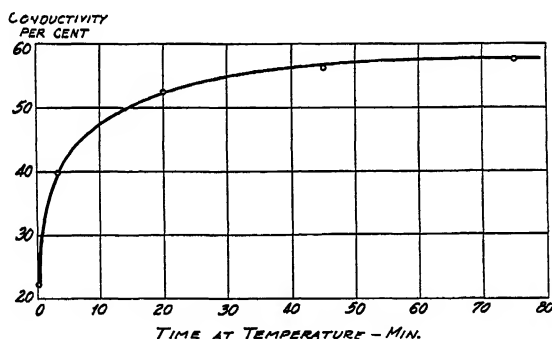


FIG. 1.—ELECTRICAL CONDUCTIVITY OF BERYLLIUM-COBALT-COPPER HEATED IN SALT BATH AT 980° F.

higher beryllium content, they offer an attractive combination of heat resistance, toughness, conductivity and hardness. It should be noted that these alloys are quenched from around 1650° F. and tempered at 850° to 900° F. The General Electric Co. has successfully applied this alloy to resistance welding electrodes²⁵. Excellent success has been found for spot-welding stainless steel, for certain types of seam-welding wheels, and for flash and projection welding electrode parts.

Another series of high-conductivity alloys, the beryllium-silver-copper group, has been investigated thoroughly by Handy and Harman. These alloys can be divided into those with more than 50 per cent silver and those with 30 per cent silver or less. In the first division a characteristic alloy is 70.44 per cent silver, 28.90 per cent copper and 0.87 per cent

beryllium. Quenched from 1400° F., this alloy will exhibit a 44 to 45 Rockwell B hardness with conductivity 53.6 per cent of copper. Holding for 6 hr. at 625° F. raises the hardness to 91.5 Rockwell B and the conductivity to 66.3 per cent of copper. These alloys have also been tried in the resistance-welding field but have not yet appeared sufficiently attractive to warrant commercial use.

Among the beryllium-copper alloys of lower silver content, a very interesting combination of tensile strength and conductivity is found. An alloy of 30 per cent silver, 1 per cent beryllium, balance copper, cold-drawn 20 per cent and then given 2 hr. at 300° C. will show a conductivity

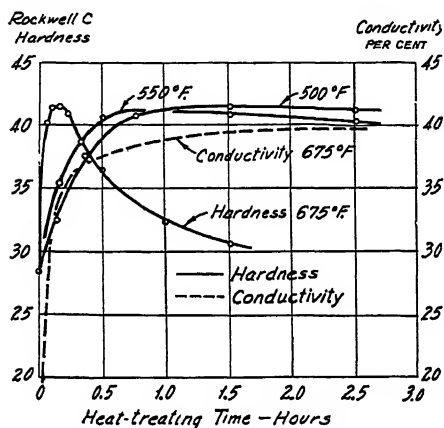


FIG. 2.—HARDNESS AND ELECTRICAL CONDUCTIVITY OF 2.25 PER CENT BERYLLIUM COPPER HEATED IN SALT BATH.

of 44.8 per cent of copper with tensile strength of approximately 160,000 lb. per sq. in. An alloy of 5 per cent silver, 1 per cent beryllium, balance copper, will show around 173,000 lb. per sq. in. ultimate tensile with 29.4 per cent conductivity after identical treatment. In contrast, 2.25 per cent beryllium-copper wire with no ternary addition shows around 140,000 to 145,000 lb. per sq. in. tensile when heat-treated to maximum conductivity of about 37 per cent, the point of highest conductivity being well beyond the point of highest tensile strength on the heat-treatment curve. Fig. 2 shows the relation between conductivity and hardness in binary beryllium copper containing 2.25 per cent beryllium.

It should be noted that the customary method of handling precipitation-hardening beryllium-copper alloys is to give the tempering treatment after the cold-work. Recent investigation of binary copper-beryllium alloys containing 1.5 per cent beryllium with the object of obtaining as high a tensile strength as possible with better than 30 per cent conductivity has shown that by giving a precipitation treatment after partial cold-work to get maximum conductivity and following this with additional cold-work quite high figures can be obtained. In this way 1.5 per cent beryllium-copper wire has been prepared that shows 190,000 lb. per sq. in. tensile strength with 31 per cent conductivity and 177,000 lb. per sq. in. with 35 per cent conductivity.

Another series of copper-beryllium alloys of interest are the nickel-copper-beryllium-manganese group, containing from 20 to 30 per cent nickel²⁶. A chill-cast bar composed of 0.4 per cent beryllium, 0.5 per

cent manganese, 20 per cent nickel and balance copper, quenched after 3 hr. at 1850° F. shows approximately a 41 Rockwell B hardness. A 2-hr. heat-treatment at 850° F. will raise this to 92 Rockwell B. If cold-worked after the quenching treatment to 82 Rockwell B, it can then be hardened by a precipitation treatment of 1.5 hr. at the same temperature to 103 to 104 Rockwell B. This is shown in Fig. 3. With 30 per cent nickel, slightly higher hardness is obtained. These alloys appear to cold-work well and show good tensile properties. Table 3 shows the tensile properties resulting from heat-treatment of an alloy of 0.4 per cent beryllium, 0.7 per cent manganese, 20 per cent nickel and balance copper, which has been considered for condenser tubing.

TABLE 3.—*Physical Properties of Cupronickel Tubing with Beryllium and Manganese Addition*

EXTRUDED, ROLLER-FORGED, AND COLD-DRAWN. QUENCHED AFTER 5 MIN. AT 1850° F. HEAT-TREATED AT 850° F. for 2 HOURS.^a

Ultimate tensile strength, lb. per sq. in.....	102,400
Yield point, 0.75 per cent, lb. per sq. in.....	67,400
Elastic limit, lb. per sq. in.....	60,100
Elongation, per cent in 2 in.....	22
Hardness, Rockwell B, 100-kg. load.....	90
Outside diameter, in.....	$\frac{5}{8}$
Wall thickness, in.....	0.049

^a Courtesy Revere Copper & Brass Co.

A ternary combination showing good precipitation-hardening with lower beryllium content is beryllium-manganese-copper²⁷. Fig. 4 shows the hardness obtainable with an alloy of 3 per cent manganese, 1 per cent beryllium, balance copper. With 5 per cent manganese, 1 per cent beryllium, a hardness as high as 37 Rockwell C has been obtained.

Commercial sale of 2.25 per cent binary beryllium-copper alloys started in this country in 1932 and has made steady progress despite the relatively high price. It is used principally as a spring metal and for bearings. There appears to be a growing appreciation of the value of forming springs in light temper and then hardening by a simple low-temperature heat-treatment to obtain more stable spring properties than can be found with steel or phosphor bronze²⁸. Electrical contact springs of beryllium copper have shown in numerous applications the ability to stand many millions of operations with no measurable loss in contact

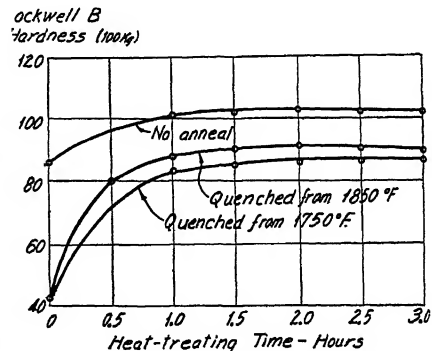


FIG. 3.—HARDNESS OF CUPRONICKEL WITH 0.4 PER CENT BE HEAT-TREATED AT 850° F. (Courtesy of Revere Copper and Brass Co.)

pressure. Users of beryllium-copper diaphragms and Bourdon-tube pressure springs report lower creep and elastic hysteresis than can be found in any other alloy commercially available. Helical springs of 2.25 per cent beryllium copper, combining a relatively low torsional modulus with high elastic limit, are proving useful where large deflections

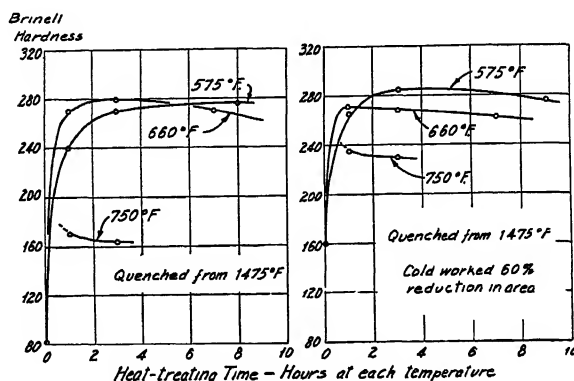


FIG. 4.—EFFECT OF HEAT-TREATMENT ON HARDNESS OF BERYLLIUM-MANGANESE-COPPER, 1 PER CENT BE, 3 PER CENT MN, 96 PER CENT CU.

are required by design engineers. For static loads they can be stressed at 100,000 lb. per sq. in. without permanent set and up to 40,000 lb. per sq. in. where fatigue is a factor²⁹.

All beryllium-copper alloys appear characterized by unusually high wear resistance. A comparison made between the 2.25 per cent material and phosphor bronze is given in Table 4, which shows that even without

TABLE 4.—Wear Test^a

COMPARISON OF WEAR OF BERYLLIUM-COPPER (2.25 PER CENT BERYLLIUM) AND PHOSPHOR BRONZE (8 PER CENT TIN) AGAINST STEEL

Size of specimen, in.....	2 by $\frac{3}{4}$ by $\frac{1}{2}$
Pressure, lb. per sq. in.....	10
Speed at bearing surface, miles per hr.....	10.3
Length of run, miles.....	200
Temperature, deg. C.....	100
Lubrication.....	None
Wear rings.....	Steel $\frac{1}{4}$ in. thick
Average depth of wear, in.: Phosphor bronze.....	0.03045
Beryllium copper as drawn.....	0.00530
Beryllium copper heat-treated.....	0.00465

^a Courtesy American Brass Co.

heat-treatment beryllium copper appears to show better than five times the wear resistance of the bronze against steel. Bearing services of moderate speed and low pressures where lubrication conditions are poor appear well handled by 2.25 per cent beryllium copper. The alloy seems to have a film-forming capacity with self-lubricating character-

istics. Bearing conditions of unusually high loads with small relative motion between shaft and bushing are also a field where the alloy has shown excellent performance. High rubbing speeds with heavy loads appear to cause seizure between a heat-treated 2.25 per cent beryllium-copper bushing and steel shaft, but not sufficient work has been done on the effect of different clearance and shaft materials. In most cases shafts of high hardness (50 Rockwell C or better) appear necessary when using 2.25 per cent beryllium alloys for bushings, because of the very high hardness of the hard crystals.

Within the last year the commercial application of cast beryllium copper to molds and dies has created considerable comment³⁰. Particularly significant is the use of cast molds in the plastic industry³¹. This development is possible because of the high physical properties obtainable in a cast and heat-treated 2.75 per cent beryllium-copper alloy and the good flowing characteristics of the metal. As will be seen from Table 5,

TABLE 5.—*Approximate Physical Properties of Sand-cast 2.75 Per Cent Beryllium Copper after Heat-treatment*

Ultimate tensile strength, lb. per sq. in.	150,000
Ultimate compressive strength, lb. per sq. in.	190,000
Elastic limit, lb. per sq. in.	135,000
Elongation, per cent in 2 in.	1
Hardness, Rockwell C.	40-42

the compressive strength of this cast alloy is higher than found in the mild steel used for most plastic molds. For parts requiring considerable ornamentation and perhaps for samples not necessitating close tolerance, this method of manufacture offers attractive savings over the usual technique employed. Experience to date appears to give evidence that the metal will stand up satisfactorily in this service.

Experiments are being carried on with the use of cast beryllium copper for metal-forming and embossing dies. Successful short runs of sterling silver knife handles and other articles have been made, using standard drop-hammer technique. The excellent surface obtained in the casting necessitates very little finishing.

2. *Beryllium Nickel*

Nickel and nickel alloys can also be made heat-treatable by adding small percentages of beryllium³². Many problems are encountered in melting and pouring these higher melting point alloys. Although copper-base alloys of beryllium can be cast by conventional methods without undue loss by oxidation, the use of specialized equipment appears at the moment essential in the production and fabrication of satisfactory beryllium-nickel alloys³³. The application of these alloys has progressed much further in Germany than in this country.

After studying a wide range of nickel-base combinations, German investigators settled on two distinct types of alloys for commercial exploitation: beryllium nickel containing 1.7 to 1.9 per cent beryllium, and a nickel-chrome-iron alloy of the 60 nickel, 15 chrome, 7 molybdenum type with 0.6 to 1 per cent beryllium. The last named material is known as beryllium contracid. Like beryllium copper, these materials show a remarkable increase in physical properties by quenching from the solid solution condition to the softest state and then reheating at an intermediate temperature. If cold-work follows the quenching treatment, the effect of the precipitation-hardening is increased. For example, binary beryllium nickel can have its tensile strength increased from 115,000 to approximately 260,000 lb. per sq. in., and beryllium contracid from 125,000 to 263,000 lb. per sq. in. by this method. The properties obtainable in these alloys are shown in Table 6.

TABLE 6.—*Physical Properties of Nickel-base Beryllium Alloys*

Alloy	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent in 100 Mm	Young's Modulus	Brinell Hardness	Specific Gravity
Beryllium-nickel:						
Quenched soft	51,000	115,000	42 9	24,900,000	140	8.1
Heat-treated from soft	109,000	176,000	25 3	26,050,000	365	
Hard-rolled	210,000	220,000	1 5	25,600,000	350	
Heat-treated from hard-rolled	213,000	260,000	8.3	27,050,000	460	
Beryllium-nickel-chrome-iron:						
Quenched soft	59,400	125,000	29.5	22,100,000	195	8.3
Heat-treated from soft	70,100	132,000	22.8	22,900,000	320	
Hard-rolled	199,000	213,000	2.0	24,000,000	320	
Heat-treated from hard-rolled	213,000	263,000	6 0	26,300,000	430	

Of particular interest in these nickel-base beryllium alloys is the very unusual toughness combined with high tensile strength. Beryllium nickel has shown values ranging from 25.2 per cent elongation at 176,000 lb. per sq. in. to 8 per cent elongation at 260,000 lb. per sq. in., with a 4-in. test length. Such properties as these surpass even good alloy steels. Another proof of the toughness of these alloys is the notched-bar impact strength. German investigators report tests on beryllium nickel showing 7 meter-kilograms per square centimeter at a 420 Brinell hardness, and 4.5 m.-kg. per sq. cm. at 460 Brinell, which are very remarkable.

As is found in most precipitation-hardening materials, a common trait of binary beryllium alloys is that after tempering to maximum hardness further heating causes an apparent coalescence of the segregated beryllide particles, resulting in softening. This limits the temperature

at which the alloys should be used continuously to the minimum point at which precipitation takes place. For material heat-treated from the soft or slightly cold-worked condition, this temperature is about 200° C. in beryllium copper; about 350° C. in beryllium nickel. For severely cold-worked material these temperatures should be reduced 25° or 50° C.

This tendency toward softening can be considerably retarded by ternary or quaternary additions. For example, the contracid beryllium or nickel-chrome-iron-beryllium alloy, mentioned above, shows an outstanding stability of hardness even after prolonged heating at the

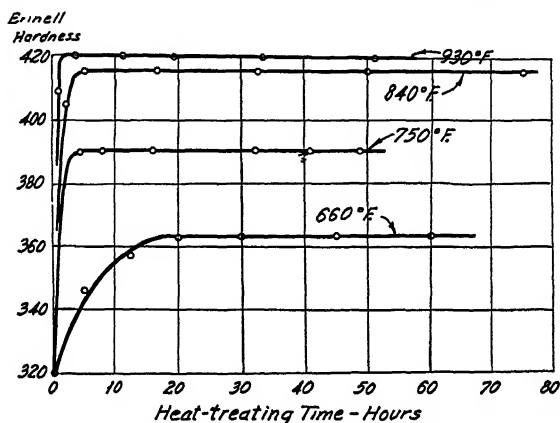


FIG. 5.—HARDNESS OF COLD-WORKED BERYLLIUM-NICKEL-CHROME-IRON.

precipitation-hardening temperature. To illustrate, in one test 30 per cent cold-worked rod stock tempered to a 415 Brinell maintained the same hardness after 80 hr. at 450°, 500° and even 550° C., as is shown in Fig. 5. For this reason, the latter alloy has shown good promise as a spring material for use at elevated temperatures, sometimes being successfully used as high as 500° to 550° C.

The alloy is also exceedingly corrosion resistant and nonmagnetic. These properties, combined with a possible elastic limit of over 200,000 lb. per sq. in., have already caused its adoption in Switzerland for main springs in high-grade watches instead of watch-spring steel.

Beryllium nickel and beryllium contracid are not being manufactured in this country, but rod, sheet, wire and tubing imported from Germany are available.

FERROUS ALLOYS

A recent paper by Dr. W. Kroll reviews thoroughly the present status of beryllium-iron alloys³⁴. About 0.5 per cent beryllium closes the gamma field in iron. Precipitation-hardening of nickel-iron and nickel-chrome-iron alloys is possible with beryllium³⁵ but additions to the 18-8 type of stainless steels result in a ferritic alloy with considerably

less corrosion resistance. An alloy of 12 chrome, 7 nickel, 1 per cent beryllium and no carbon can, however, be hardened to the high value of 675 Brinell.

An austenitic beryllium-iron alloy of the type 30 chrome, 30 nickel, 1 per cent beryllium can be cold-rolled and then tempered to 500 to 550 Brinell. This shows 235 Brinell in the soft condition. Invar steels with 36 per cent nickel can be hardened to 365 Brinell with 1 per cent beryllium.

Mention should be made of the interesting work in France of Joseph Laissus³⁶ on the casehardening of iron and iron alloys with beryllium by cementation. He claims that he has obtained by this means a surface hardness on a 0.09 per cent carbon steel of 1506 Vickers, which is considerably greater than can be obtained by nitriding.

A recent investigation of the application of beryllium to nitriding alloys has shown that by adding around 1 per cent beryllium to nickel-iron alloys, with or without chromium, a material is obtained that can be precipitation-hardened and at the same time given a hard case³⁷.

PRECIOUS-METAL ALLOYS

1. *Beryllium Silver*

Some investigators have claimed that small additions of beryllium to fine silver and sterling silver resulted in a noticeable increase in their tarnish resistance³⁸. Investigations made in this country³⁹ and in Germany have indicated that while there is a selective difference in favor of small beryllium additions in the order of 0.5 per cent when subjected to certain types of mild tarnishing mediums, this is not so apparent when the alloys are subjected to other tarnishing conditions to which silver is likely to be subjected in use. A further disadvantage is that there is apparently very limited, if any, solid solubility of beryllium in silver the result being a surface somewhat difficult to polish. Accordingly no commercial development has taken place in these alloys.

2. *Beryllium Gold*

The addition of beryllium to gold appears to have decided hardening effect, 1 per cent beryllium giving fine gold an as-cast hardness of approximately 85 Rockwell B and 5 per cent beryllium a hardness of 122 Rockwell B, or well over 400 Brinell. However, with much over 0.5 per cent beryllium these alloys become too brittle to work.

A study of the possible addition of beryllium to some 14-kt. golds similar to those used for pen points has not proved successful because of similar embrittlement. An alloy of 75 per cent Au, 13.5 per cent Cu, 10 per cent Ag and 1.5 per cent Be has been found to have on slow cooling an as-cast hardness of 109 Rockwell B (approximately 330 Brinell).

An interesting fact concerning all the beryllium-gold alloys is the apparent presence of a eutectic at approximately 0.5 per cent beryllium, which melts in the neighborhood of 1070° F.

Commercial application of beryllium-gold alloys appears limited to possible use for dental inlays and for low-melting gold solders.

DEOXIDATION AND DESULFURIZATION WITH BERYLLIUM

The affinity of beryllium for oxygen and sulfur is so great that the metal has very useful properties as a deoxidizer and desulfurizer⁴⁰. Beryllium will displace even the active reducing elements such as aluminum and calcium from their oxygen compounds and accordingly can be considered among the best available deoxidizers. Table 7 gives an interesting comparison with other elements in this respect.

In Germany beryllium is successfully used in amounts between 0.01 and 0.02 per cent to obtain sound, dense, high-conductivity sand castings⁴¹.

In this country several successful experiments have been run on the use of very small amounts of beryllium to increase fluidity and reduce porosity on castings requiring sharp detail on the as-cast surface. Trials have also been made to determine what conductivity could be obtained

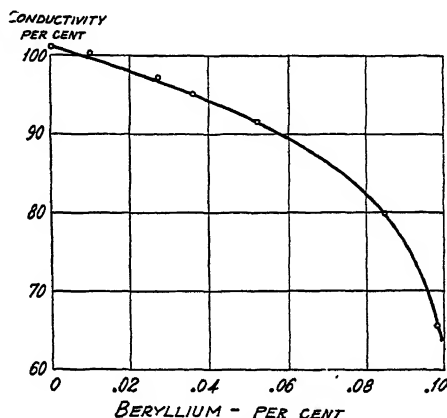


FIG. 6.—EFFECT OF BERYLLIUM ON ELECTRICAL CONDUCTIVITY OF ANNEALED COPPER. (Courtesy of S. Skowronski, Raritan Copper Works.)

in annealed copper wire deoxidized with beryllium. The effect of additions running from 0.01 to 0.1 per cent on the conductivity are given in Fig. 6, showing that somewhat better than 100 per cent of the copper standard can be obtained with 0.01 per cent beryllium. Bending tests after a hydrogen anneal showed that the copper was completely deoxidized with a 0.01 per cent addition, but in these tests the copper was somewhat gassy and did not shrink entirely satisfactorily until about 0.05 per cent beryllium was added.

As a desulfurizer of steel baths, the action of beryllium is astonishing⁴². As is well known, desulfurization should best be carried out both from a chemical and physical point of view. Chemically the affinity of beryllium for sulfur is similar to that of Cr, Zr and Ti, but much stronger. Being bivalent and having an atomic weight of 9.02, beryllium will take up a greater weight of sulfur per gram of its own weight than any other metallic element, as is shown in Table 7. The low specific gravity and

apparent decreasing solubility at decreasing temperatures of the beryllium sulfide formed appears to enable its removal by a suitable slag. As beryllium is soluble in iron and has a high volatilization point, its action is said to be more effective than that of calcium or lithium. Of perhaps

TABLE 7.^a—*Scavenging Power of Beryllium for Oxygen and Sulfur Compared with Certain Other Elements*

Element	Grams Oxygen that Combine with One Gram of Element	Kilogram-calories Set Free when One Gram of Element Combines with Oxygen	Grams Sulfur that Combine with One Gram of Element
Be	1.774	15.23	3.554
Na	0.348	2.18	0.697
K	0.204	1.11	0.410
Rb	0.094	0.46	0.188
Cs	0.060	0.31	0.120
Li	1.152	10.33	2.309
Mg	0.658	6.00	1.320
Ca	0.399	3.72	0.800
Sr	0.182	1.61	0.366
Ba	0.116	0.97	0.234
Al	0.890	7.05	1.783
Zn	0.245	1.27	0.491
Mn	0.292	1.707	0.583
Si	1.140	6.80	^b
Ti	0.668	4.56	^b
P	1.289	5.78	^b
Zr	0.350	2.90	0.351

^a H. Osborg: Lithium, Theoretical Studies and Practical Applications. Electrochem. Soc., Inc., 1935.

^b Not determined.

greater interest is the fact that if the beryllium sulfide formed is allowed to remain in the melt there seems to be no hot shortness even with a surprisingly high sulfide content. In one laboratory test a steel with 0.76 per cent beryllium sulfide was easily rolled down to thin sheet.

It should be mentioned that pure nickel can be made rollable without a magnesium and manganese addition by the use of small amounts of beryllium. German investigators have reported a nickel 10 to 15 per cent softer than the best available commercial grades of pure nickel through the sole addition of 0.02 per cent beryllium.

CONCLUSION

Pure beryllium is not quoted in this country but master alloys with copper, nickel and iron are sold at prices ranging from \$30 to \$40 per pound of contained beryllium with the base metal at the market price. Wrought 22.5 per cent beryllium copper is offered in standard commercial

sizes and shapes at prices ranging from 97¢ to \$1.50 per lb., by several companies fabricating nonferrous alloys.

As in the early days of the aluminum industry, the cost of producing small quantities of beryllium has been high. However, through untiring research and close cooperation with the German investigators in the same field, important strides are being made towards simplifying production processes. Although in all likelihood beryllium will remain a relatively expensive metal, the price has already been reduced from \$200 to \$30 a pound since 1929, and there is every assurance that with increased demand this can be brought down to less than half the present level.

SUMMARY

The oxide of beryllium was identified in 1797, but until recent years only a few grams of metal were produced. The history of the many attempts to find a satisfactory method of extraction is well covered in the published work of Siemens and Halske.

Although of very low specific gravity (1.84) and having a higher rigidity than steel, there appears little hope for the use of pure beryllium as an engineering material. The metal can be given some hot-work but appears brittle at room temperature when made in the highest purity so far possible on an industrial scale.

Alloys of beryllium with light metals have not yet proved commercially interesting, but growing uses are being found for small additions of the element to copper and nickel alloys.

In this country beryllium copper containing approximately 2.25 per cent beryllium is becoming well established as an outstanding spring material. A recent application of the cast alloy to dies for molding plastics appears to offer promise. Ternary and quaternary alloys enabling good precipitation-hardening with as little as 0.2 per cent beryllium are being developed. Of particular interest is the beryllium-cobalt-copper alloy, which after heat-treatment combines a conductivity of about 50 per cent of copper with a hardness of 96 to 98 Rockwell B.

In Germany considerable investigation has been made of nickel-beryllium alloys. Nickel with 1.8 per cent beryllium can be heat-treated to values as high as 260,000 lb. per sq. in. tensile strength with 7 to 8 per cent elongation. A nonmagnetic, highly corrosion-resisting beryllium-nickel-chrome-iron alloy is being used for heat-resistant springs and even for winding springs in watches.

Iron alloys, particularly nickel-iron and nickel-chrome-iron, can also be made precipitation-hardening by adding beryllium.

Claims have been made that a small beryllium addition to silver gives increased tarnish resistance but the improvement is not found under all testing conditions. Beryllium hardens gold and gold alloys but seriously impairs their ductility.

The high affinity of beryllium for oxygen and sulfur has prompted numerous experiments on its use for deoxidation and desulfurization. Excellent high-conductivity copper castings can be made with small beryllium additions. Steel melts are successfully desulfurized with beryllium and alloys with unusually high sulfide content are still rollable when beryllium is added.

Beryllium alloys, both as ingot material and as sand castings, are manufactured in the United States. Metallic beryllium is not quoted but master alloys with copper, nickel and iron are currently sold at a price of \$30 to \$40 per pound of contained beryllium. Wrought beryllium copper is available in regular commercial sizes and shapes through several fabricators at prices around 97¢ to \$1.50 per pound. Increased demand will reduce the price of beryllium alloys materially.

ACKNOWLEDGMENT

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37. W. Kroll: U.S. Patent 2029724.
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Notes on the Crystallization of Copper*

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(Chicago Meeting, October, 1935)

THE time-honored description of the growth of metal crystals to form polycrystalline aggregates is one in which two important steps are considered: (1) nucleation, and (2) dendritic growth, each dendrite starting from its individual nucleus and resulting (upon slow cooling, assuming no solid phase changes) in a macrograin. This picture of the process of crystallization is incomplete, and it is with the hope of enlarging upon it that the following summary and correlation of experimental results are given.

MOSAIC STRUCTURE

For an exact definition of the mosaic structure of metal crystals—if, indeed, one can be found that will hold for all metals—one must await the results of much experimental work in this field. The writer's investigations have been confined almost entirely to copper and a few of its alloys. The following terms are proposed, and will be used in this report:

*Macromosaic Structure*¹.—Large-scale mosaic structure; more specifically, mosaic structure of a scale large enough to produce splitting of Laue spots on back-reflection Laue X-ray patterns². The deviation from exact parallelism of neighboring macromosaics varies from a few minutes to a few degrees³. Just as there are no exact dimension limits for macrograins, so the dimensions of a macromosaic vary considerably. Macromosaic structure may often be seen on copper single crystals if they are examined carefully with critical illumination⁴. However, back-

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¹ It is believed that this term fits more readily into metallurgical terminology, and describes the structure more accurately, than does the more restrictive term "lineage structure" proposed by Buerger, and used by the writer in a former publication.

² A. B. Greninger: Determination of Orientation of Metallic Crystals by Means of Back-reflection Laue Photographs. *Trans. A.I.M.E.* (1935) **117**, 61.

³ A. B. Greninger: Crystallographic Uniformity of Lineage Structure in Copper Single Crystals. *Trans. A.I.M.E.* (1935) **117**, 75.

⁴ Probably the most satisfactory etching reagent for detecting small orientation

reflection Laue X-ray patterns will give more definite information (from a limited area) than can be secured from visual examination.

*Micromosaic Structure*⁵.—Mosaic structure of too fine a scale to produce splitting of back-reflection Laue spots, but which is evidenced by the broadening of the diffracted X-ray beam. The Laue spots may be

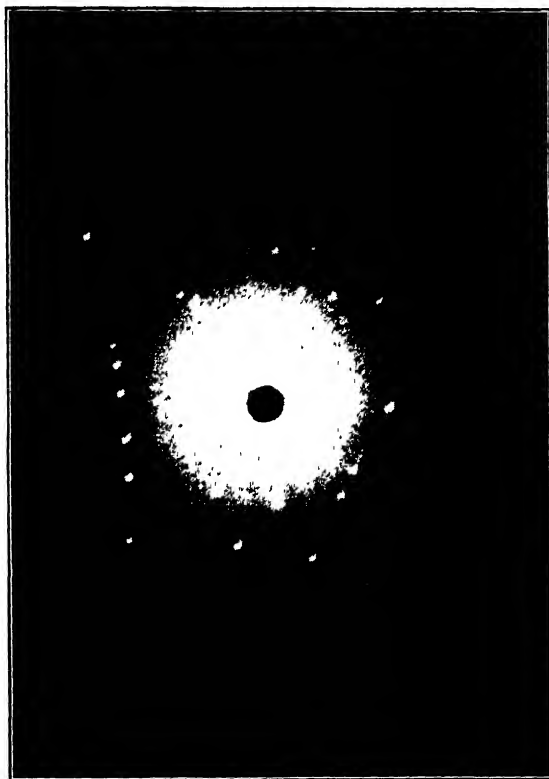


FIG. 1.—BACK-REFLECTION LAUE PATTERN OF NUCLEUS OF A COPPER CRYSTAL, SHOWING NEAR-SHARP REPRODUCTION OF X-RAY FOCAL SPOT.

broadened symmetrically or unsymmetrically. Also, unsymmetrical distortion of the beam may occur without any perceptible broadening.

A few statements may be made concerning mosaic structure in general:

1. In copper single crystals grown from the melt, the macromosaic structure is, in general, more pronounced in rapidly solidified crystals.

differences in copper is $\text{HNO}_3 + \text{Ag}$. This reagent develops sharp, bright $\{111\}$ facets and $\{111\}$ traces on copper and on all copper alpha solutions with which it has been used.

⁵ Micromosaic structure may also be of submicroscopic dimensions, and the term "micromosaic" will be used with this additional significance.

2. The addition of small amounts of silver (0.5 to 3 per cent) to copper produces single crystals having a much more pronounced macromosaic structure than have pure copper crystals grown under identical conditions. (Compare Figs. 1 and 2.)

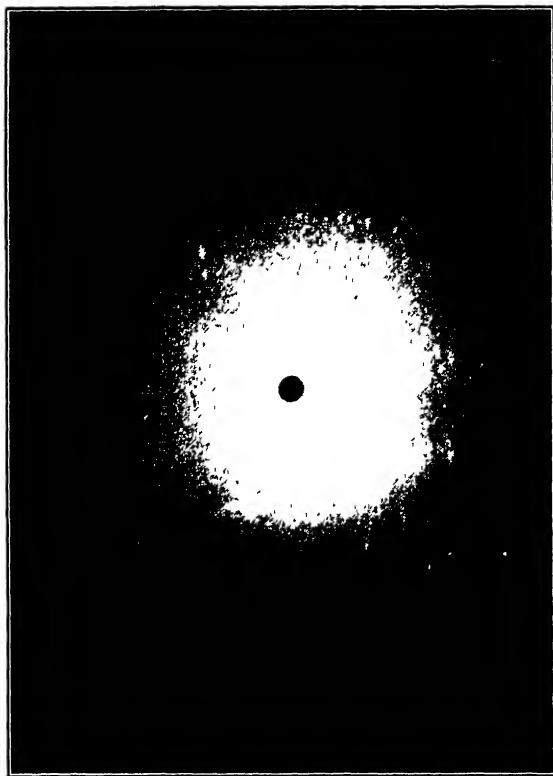


FIG. 2.—BACK-REFLECTION LAUE PATTERN OF NUCLEUS OF A $\text{Cu} + 3$ PER CENT Ag CRYSTAL, SHOWING PRONOUNCED MACROMOSAIC STRUCTURE.

3. In general, macromosaic structure is most pronounced in the region near the nucleus, in crystals grown from the melt. However, it is only in a few nucleus photographs that near-perfect reproductions of the focal spot of the X-ray tube have been obtained.

4. Photographs taken on the most carefully prepared copper crystals⁶ may or may not show macromosaic structure, but most of them show broadening of the Laue spots to a greater or less extent. Likewise, strain-anneal copper crystals are characterized by the absence of macromosaic structure.

⁶ The top hemispherical surfaces of such crystals show a pattern somewhat resembling mud cracks. Diffraction patterns of these surfaces produce Laue spots having lines devoid of blackening which correspond to the surface "channels."

5. Patterns in which the spot detail of macromosaic structure is sufficiently sharp to permit interpretation suggest that this structure is crystallographically uniform—the two lattices can be superimposed by rotating one a few minutes or degrees ($5''$ or $10''$ to 8°) around the common symmetry axis.

6. There appears to be little or no connection between dendritic structure and macromosaic structure in copper.

7. Once a macromosaic has formed near the nucleus (or at any point in the crystal), it may continue to impress its slightly different orientation on a section of the growing crystal, and appear in the final crystal as an irregular column—the result of columnar growth.

SIGNIFICANCE OF MOSAIC STRUCTURE

Possibly the most important point on which physicists disagree in their theoretical interpretations of the mosaic structure concept is in deciding whether the phenomenon is fundamental or merely accidental, whether it is intimately connected with all crystallization as a process or can be considered as belonging only to "imperfect" crystals. For, if mosaic structure is to be considered responsible for such fundamental processes as plastic deformation⁷, its formation or growth must be an integral part not only of crystallization but of recrystallization as well.

It is unfortunate that most of the studies that have been made of the behavior of single metal crystals were carried out before the study of the structure of the "single crystal" had progressed very far. A few publications have appeared dealing with differences in properties of crystals of the same metal⁸. Dehlinger⁹ has reported that stress-strain curves (tensile) of strain-anneal aluminum crystals show a marked inflection corresponding to a yield point, while Bridgman crystals of the same

⁷ G. I. Taylor: The Mechanism of Plastic Deformation of Crystals. *Proc. Royal Soc.* (1934) A145, 362–405.

⁸ Recent work in the field of experimental physics has resulted in the classification of metal crystals as either (1) single crystals, or (2) optical mosaics. See H. K. Schilling: Mosaic Crystals of Zinc. *Physics* (1934) 5, 1; W. J. Poppy: Electrical Resistivity of Single Crystals and Optically Mosaic Zinc Crystals. *Phys. Rev.* (1934) 46, 815–821. C. A. Cinnamon: The Thermal Resistivity and the Wiedemann-Franz Ratio of Single Crystal Zinc. *Phys. Rev.* (1934) 46, 215–221.

The assumption evidently is made that if mosaic structure cannot be seen it does not exist. Cinnamon states: "The production of optical mosaics having a higher conductivity than single crystals is a very strong argument against supposing that the highest attainable conductivity is indicative of the most nearly perfect crystal." No attention has been given to the fact that macromosaic structure may be "optically invisible" and yet may be shown to be present if proper X-ray technique is used.

⁹ U. Dehlinger: Nachtrag zu Neue Ansätze zur Rekristallisationstheorie. *Metallwirtschaft* (1933) 12, 298–299.

metal undergo permanent deformation under very small load. Wiest and Dehlinger¹⁰ conclude that the size of mosaic blocks is of fundamental importance in explaining behavior differences of crystallized and recrystallized metal crystals.

More experimental data of this kind are needed. Whether or not mosaic structure is a common property of all crystals, it must be admitted that it is a factor that must be considered in any exact measurements of the properties of metal crystals. An evaluation of the effects of the presence (or absence) of *macromosaic* structure should eventually lead to an understanding of the perhaps more fundamental *micromosaic* structure.

POLYCRYSTALS OF COPPER

The question might well be asked: In what way does a macromosaic differ from an ordinary macrograin, and is there any clear distinction between the two? It is well known that when metal single crystals are being prepared by the Bridgman method, occasionally for unknown causes a product is obtained that apparently consists of two or three grains instead of one crystal. Might not these grains derive their orientation (nucleus) from the parent nucleus through a disturbance similar to that producing the near-parallel orientation of a macromosaic? It has been generally assumed that these extra grains are formed when the original nucleus does not have an orientation favorable for growth¹¹. However, the more pertinent question at this point is whether these grains are primary (nucleus derived from nucleation along the walls of the mold) or secondary (nucleus derived from a disturbance in the primary grain lattice).

PREPARATION OF SPECIMENS

A few copper specimens used in this investigation were prepared by the same procedure used in making single crystals of copper¹², but with higher solidification speeds. Because of the difficulty of obtaining anything but a single crystal with this apparatus, most specimens were prepared by melting and solidifying high-purity copper in a covered graphite crucible in an induction furnace. The crucible was so arranged in the furnace that upon cooling solidification would proceed from the bottom upwards. The temperature gradient was high—about 200° C. in 2 in. when the bottom of the crucible was at 1100° C. The resulting

¹⁰ P. Wiest and U. Dehlinger: Vergleich der Aushärtung einer Gekneteten und einer Gegossenen Legierung. *Ztsch. f. Metallkunde* (July, 1934) **26**, 150–152.

¹¹ C. H. Mathewson and K. R. Van Horn: Directed Stress in Copper Crystals. *Trans. A.I.M.E.* (1930) **89**, 66.

¹² Reference of footnote 3, 2.

specimens consisted in a rod of copper containing from two to six large grains. Such a specimen, grown to eliminate as much as possible the formation of two or more primary nuclei, will be called a *polycrystal*.

The orientations of all grains in several polycrystals were determined by means of back-reflection Laue X-ray patterns. The polycrystals were then ground and polished to expose one or more faces for examination of dendritic structure.

RESULTS

The orientation relationships of 15 pairs of neighboring grains in seven different polycrystals were determined. Of these, six pairs of neighboring grains were found to have an octahedral twin¹³ relationship to one another. These twins are of two general types: (1) those in which a composition plane is the twinning plane, and (2) those in which the twinning plane is not a composition plane. A twin of the first type may be seen in Fig. 7. Fig. 3 is a photograph of a twin of the second type, and its orientation is plotted stereographically in Fig. 4¹⁴.

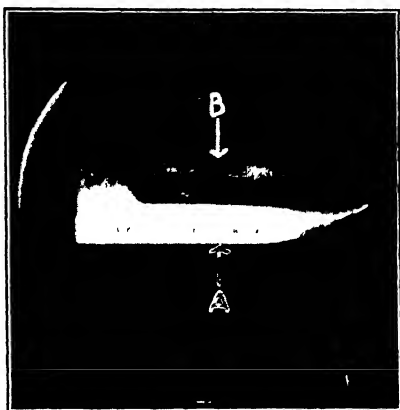


FIG. 3.—OCTAHEDRAL TWINS IN A COPPER POLYCRYSTAL (BOTTOM SECTION). NATURAL SIZE. ETCHED IN $\text{HNO}_3 + \text{Ag}$. Specimen showed no dendritic structure after polishing and etching. Horizontal boundary does not correspond with twinning plane trace.

Of the remaining pairs of orientation relationships, several were close to an octahedral twin relation; that is, the twin relation could be obtained by rotating one lattice a few degrees about an axis $[uvw]$. Fig. 6 is an illustration of such a relation, in which the axis of rotation lies in the projection plane. Three of the orientation pairs are closer to a parallel relation than to a random one. Three of the eight rotation axes correspond ($\pm 1^\circ - 1.5^\circ$) to symmetry axes.

¹³ The spinel-twin relationship of large twins may be determined with an accuracy of 5 or 10 min., if the perfection of the crystal permits, from a back-reflection Laue photograph taken in such a way that the X-ray beam strikes the grain boundary, and a projection of one of the common planes in the twin relation is obtained on the X-ray pattern.

¹⁴ Grains resembling twins have been observed on surfaces of copper and silver castings; so far as the writer knows, the twin relation in castings has never been proved. See M. L. V. Gayler: discussion of paper by C. O. Bannister, *Studies on the Crystallization of Gold from the Liquid State*. *Jnl. Inst. Metals* (1929) **42**, 146-147.

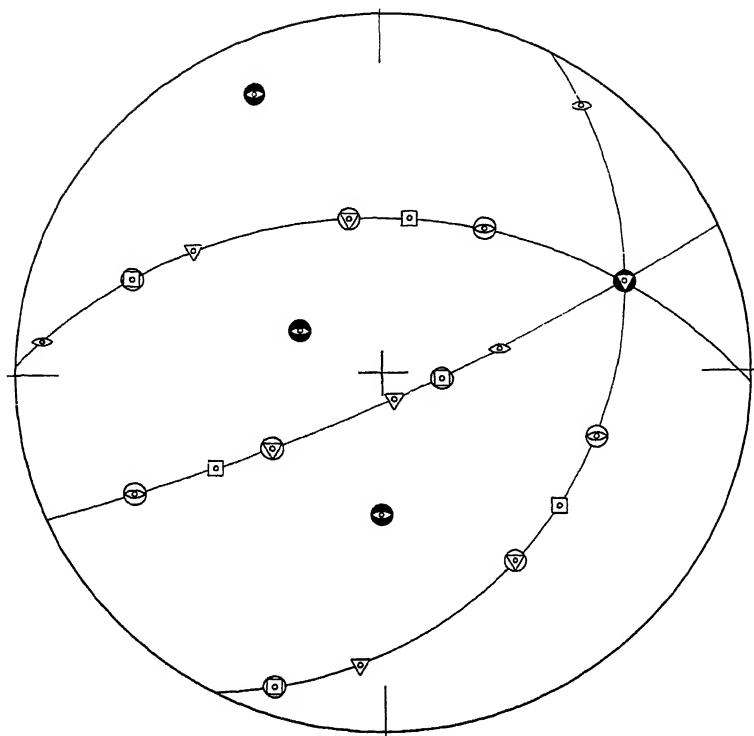


FIG. 4.—STEREOGRAPHIC PROJECTION OF ORIENTATION OF GRAINS A AND B OF FIG. 3.
 $\square = \{100\}$ $\circ = \{110\}$ $\triangle = \{111\}$.

Plain symbols = grain A poles; encircled symbols = grain B poles; black-encircled symbols = poles common to both grains. Great circles = projections of the three common $[110]$ axes of the twin relation.

TABLE 1.—*Rotation of Orientation Pairs*

Number of Orientation Pairs	For Twin Relation ^a Rotation Required around Axis $[uvw]$	For Parallel Relation ^a Rotation Required around Axis $[uvw]$
6	Spinel twin relation	
1	$16^\circ [uvw] = [111]$	
1	16°	
1	8°	
1	15°	
1	$23^\circ [uvw] = [110]$	
1		$8^\circ [uvw] = [111]$
1		23°
1		41°
1		$15^\circ [uvw] = [111]$

^a Relationships are accurate to $\pm 1^\circ$ – 1.5° . Macromosaic structure usually interferes with higher accuracies.

The specimen of Fig. 8 illustrates the use of both dendritic structure and orientations in determining the probable growth history of a polycrystal¹⁵. Dendritic structure is helpful because when well developed it defines the grain orientation (with respect to two dimensions) at the time of crystallization. There can be no doubt that dendrite axes in copper coincide with the crystallographic axes of the lattice during growth. Fig. 8 illustrates the changes that may occur subsequent to crystallization. For example, the long dendrite axis of grain *B* corresponds, as it should, with the location of a {100} trace determined from the orientation; this dendrite can be seen to extend over into grain *A*₁. Subsequent to solidification, a part of grain *B* has been assimilated by grain *A*₁. Likewise, grain *A*₂ has assimilated a portion of grain *C*. *A*₁ and *A*₂ are views of the same grain on opposite parallel faces; the grain orientation demands a vertical {100} trace, and this is fulfilled on *A*₂ face and for a short distance on the *A*₁ face, but the long dendrite on the latter face is inclined about 3°—the grain corresponding to this long dendrite has been completely assimilated by the *A*₂ dendrite orientation.

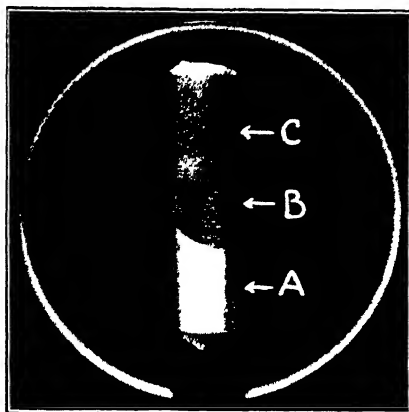


FIG. 5.—COPPER POLYCRYSTAL. NATURAL SIZE. ETCHED IN $\text{HNO}_3 + \text{Ag}$.

The small twins that may be seen in grain *B* (Fig. 8) have the twinning plane (111) as one composition plane. The other straight-line boundary corresponds with a trace of one of the common {110} planes of the twin relations. This is the usual occurrence in large annealing twin bands when the bands do not extend completely across the grain (see Fig. 9).

All grains definitely shown to have suffered partial assimilation have characteristic, smooth, undulating boundaries. "Growth twins," on the other hand, have straight-line or step-like boundary lines. Probably all grains immediately after solidification have boundaries that approach the nearly straight lines characteristic of columnar growth and, conditions permitting, these boundaries are later changed by movements tending to reduce surface area to a minimum. Evidently the relative stability of the twin relation opposes this reduction of surface energy.

¹⁵ The phenomenon of granulation of dendrites of pure metals other than iron is mentioned in only one of the several well-known treatises on physical metallurgy. (See, A. Sauveur: *Metallography and Heat Treatment of Iron and Steel*. Univ. Press, Cambridge; 3d ed., 1926, 155.) The occurrence of cell structures and intersecting sets of "apparent crystal boundaries" on surfaces of castings has been studied. (See, Bannister, reference of footnote 14; and C. H. Desch: *The Chemistry of Solids*, Chap. 4. Cornell Press, 1934.)

DISCUSSION AND THEORETICAL CONSIDERATIONS

It has been shown that macrograins in a copper polycrystal may be defined with respect to orientation relationships of neighboring grains as: (1) common symmetry axis (macromosaic relation), (2) spinel twin, (3) near-twin, (4) near-parallel, and (5) random, or no relation. These relationships favor the suggestion that most macrograins in polycrystals

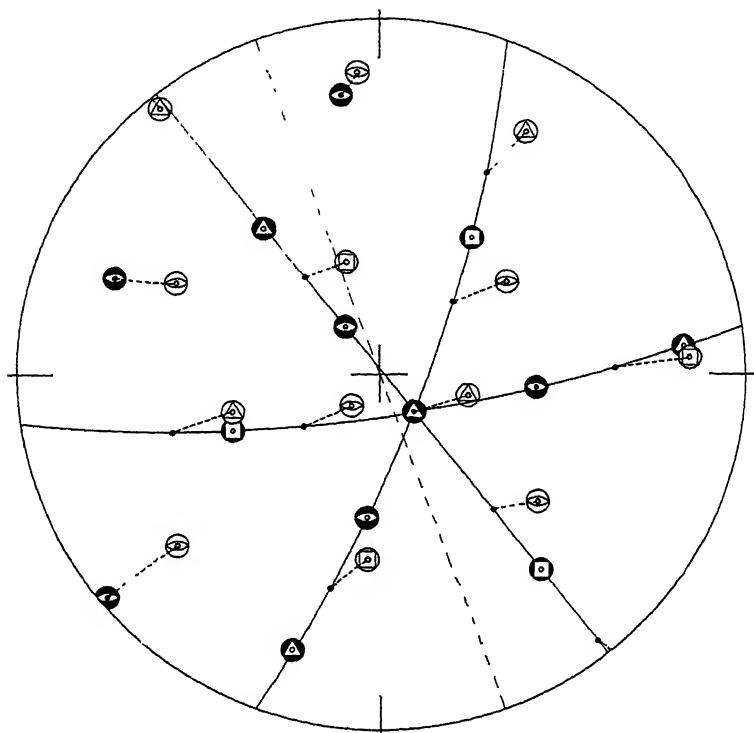


FIG. 6.—STEREOGRAPHIC PROJECTION OF ORIENTATIONS OF GRAINS *B* AND *C* OF FIG. 5 ON PLANE CONTAINING ROTATION AXIS $[uvw]$ (BROKEN LINE). $\square = \{100\}$ $\circ = \{110\}$ $\Delta = \{111\}$.

Light symbols = grain *C* poles; dark symbols = grain *B* poles; Great circles = projections of three of the $[110]$ directions of grain *B*.

C is rotated 16° about $[uvw]$ to produce twin relation. (Grains *A* and *B* of Fig. 5 have a similar relation, with 8° rotation required for twin relation.)

are secondary; that is, their nuclei are derived from disturbances in the primary grain lattice.

The occurrence of twins (and of only one type of twin relation) in a slowly solidified pure metal implies that the twinning mechanism may be more intimately connected with all types of grain formation than has been assumed heretofore.

As an aid in assembling and correlating these experimental results, the following hypothetical description of the crystallization of copper is

given. It does not necessarily represent the writer's beliefs; it is merely one of two or three ways in which the results may be interpreted, and admittedly it is incomplete.

1. Subsequent to primary nucleation, all deviations from exact parallelism begin as a lattice movement of which the resultant may be described as a rotation about a symmetry axis¹⁶.

2. This movement is the result of a disturbance; minute disturbances occur continuously during, and for some time after, crystallization, and have as an initial result micromosaic structure.

3. These minute disturbances may be cumulative and, depending upon the conditions surrounding them (i.e., deviation from equilibrium conditions), the resultant movement may (1)

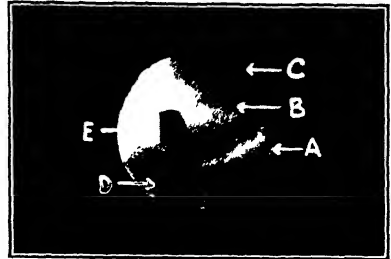


FIG. 7.—TOP OF A POLYCRYSTAL. TWICE NATURAL SIZE. ETCHED IN $\text{HNO}_3 + \text{Ag}$.

B and *C* are twins, with composition plane = twinning plane. *D* is the top of a columnar macromosaic, having common $[111]$ with *A*. *E* and *A* are near-twins; rotation axis = $[111]$.

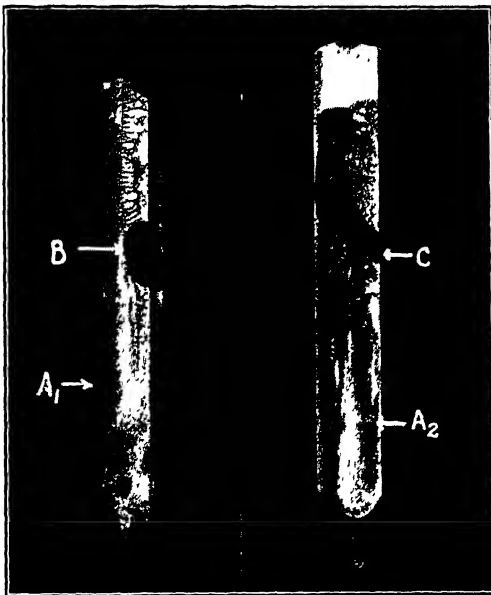


FIG. 8.—VIEWS OF ONE POLYCRYSTAL ON OPPOSITE PARALLEL FACES. NATURAL SIZE. ETCHED IN $\text{HNO}_3 + \text{Ag}$.

be small, terminating in the formation of a macromosaic, or (2) go to completion, resulting in the formation of a twin, or (3) stop somewhere

¹⁶ It is interesting to note that Barrett has reported [C. S. Barrett, H. F. Kaiser, and R. F. Mehl: Studies upon the Widmanstätten Structure, VII. *Trans.*

between these two extremes; that is, movements may begin as a rotation about one axis and be followed by subsequent rotation about another, attaining a near-parallel, near-twin, or a "random" arrangement¹⁷.



FIG. 9.—LARGE ANNEALING TWINS IN COPPER. THREE TIMES NATURAL SIZE. ETCHED IN $\text{HNO}_3 + \text{Ag}$.

Produced by cold-working a single crystal to 50 per cent reduction of area (octagon shape), and annealing 100 hr. in nitrogen atmosphere at 1060°C .

4. If the resulting lattice disturbance extends to the solid-liquid interface, the newly formed orientation may act as a nucleus for further growth, producing growth twins, elongated or columnar macromosaics, etc.

5. Favorable conditions for twin formation are large disturbances with "near equilibrium conditions." Thus, grains in slowly solidified polycrystals will tend to become twins; grains in rapidly solidified polycrystalline aggregates (as castings) will tend toward the near-parallel arrangement.

6. A grain, once crystallized, may later (1) be completely assimilated by a neighboring grain, (2) be partially assimilated by a neighboring grain, or (3) granulate. These movements may also occur upon subsequent high-temperature annealing of a polycrystal. Grains in copper that has passed tranquilly

A.I.M.E. (1935) 117, 39] that numerous matrix crystals in silver-rich Ag-Cu alloys undergo fragmentation after partial precipitation, producing a new set of orientations which may be derived from the original by rotations in two directions of $42^\circ \pm 5^\circ$, about [100], [010], and [001] of the original lattice. This relationship is essentially the same as that which Bøggild has found to exist between the kamacite and the octahedrite structure of meteoric irons [O. B. Bøggild: *The Meteoric Iron from Savik near Cape York, North-Greenland. Sætertryk af Meddelelser om Grønland* (1927) 74, 1-30]. Preliminary results by the present writer, applying the back-reflection Laue method to sections of the Cases Grandes meteorite, confirm Bøggild's conclusions; viz., there is no exact relation between the {111} planes of the octahedrite and the {110} planes of the kamacite, but there are three groupings of kamacite orientations, which may be produced by rotations of $45^\circ \pm 10^\circ$ about the major axes of the octahedrite.

It should be noted that a rotation about a fourfold symmetry axis cannot produce the octahedral twin relation. It is probable that this orientation relationship defined independently by Bøggild and Barrett may be closely related to twinning in regard to mechanism.

¹⁷ In all orientation pairs not having a common symmetry axis, it was observed that one orientation (A) could always be derived from the other one (B) by a rotation of A about an axis of symmetry followed by a rotation of A_1 about an A_1 symmetry axis. This condition demands a symmetry pole (of A) on the stereographic plot

from the liquid to the solid state are not thermodynamically stable for all temperatures within the crystalline phase range.

7. After a macromosaic nucleus has been formed, dendritic growth may or may not determine the boundary limits of the resulting columnar macromosaic. Dendritic structure is regarded merely as the result of more rapid proceeding of crystallization in certain crystallographic directions; preferential growth has impurity segregation as a natural result.

ACKNOWLEDGMENT

The writer wishes to thank Dean H. E. Clifford, Prof. Albert Sauveur, Dr. H. H. Lester, and the Harvard Engineering School for having made this research possible, through facilities, aid and advice. Dr. C. S. Barrett very kindly made a critical review of the manuscript.

DISCUSSION

(*W. P. Sykes presiding*)

C. S. BARRETT* AND R. F. MEHL,† Pittsburgh, Pa. (written discussion).—The author is to be complimented on the method by which he has obtained experimental facts on an interesting and important subject. It occurs to some of us, however, that the author's interpretation of his data is open to criticism in a number of particulars; we presume he will welcome such criticism, for he implies in the paper that he himself is not wholly satisfied with his interpretation.

Let us consider the hypothesis that all deviations from perfect parallelism begin as a lattice movement equivalent to rotation about a symmetry axis, either going to completion, forming a twin, or stopping short of the twin orientation. It should be pointed out that this conception of twin formation is a radical departure from that accepted by crystallographers in general, which might be expressed in the words of Tutton as follows: "... the twin is simply the expression of the fact that the growth of the crystal has occurred simultaneously according to two distinct but intimately related orientations, owing to the molecules of the substance in the act of crystallization taking up two alternative positions with equal facility."

A measure of caution is necessary in postulating any macromosaic mechanism or twin mechanism as a substitute for the theory of a Widmanstätten mechanism as the author has done in footnote 16, and as he has done in his recent note to *Nature* (June 1, 1935, page 916). No type of lattice disturbance in either one of the two phases involved in a Widmanstätten structure can alone account for the orientation relationships of that structure; it is always necessary to postulate a mechanism relating the orientation of one phase to that of the other. It should be noted that the orientation relations quoted here for meteorites are in disagreement with those found in meteorites by Young and recently in this laboratory by Derge, as well as those in iron-

located at the intersection of two similar zonal curves of *A* and *B*. However, the relation must be investigated with higher accuracies and a large number of specimens before it can be established. The relation cannot be considered definite unless it is found to hold after limits of error are reduced to about one-fourth degree.

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nickel alloys noted by Nishiyama, by Wasserman, and in the structurally similar iron and iron-carbon studies by Kurdjumow and Sachs, by Mehl, Barrett and Smith, and by Mehl and Smith. Neither twinning on (111) or (112) planes nor such twinning followed by any reasonable amount of scattering can account for the Widmanstätten relationships reported by these investigators; nor can it account for the orientations of ferrite in pearlite found by Mehl and Smith. It was shown by Barrett, Kaiser and Mehl that twinning was very unlikely in the reoriented matrix of silver-rich silver-copper alloys, and that a more reasonable explanation of the phenomenon was recrystallization with preferred orientation.

Caution is also necessary in interpreting Table 1 of Dr. Greninger's paper. For example, one might ask the following question: Excluding the six examples of twinning, does not Table 1 represent a purely chance distribution of orientations? Let one crystal of each of the pairs be fixed in a standard orientation and the other crystal of each pair be rotated at random with respect to it; the various axes of rotation will then be distributed at random over the surface of the projection sphere. We may then compute the probability that an axis will lie within 1.5° of a [100], [110] or [111] pole of the fixed crystal by computing the ratio of the total area of the 26 circular regions about these poles on the projection sphere to the total area of the sphere. The ratio is $\frac{1}{516}$. This is to be compared with the fraction of entries in column 3 of Table 1 for which an axis $[uvw]$ is listed, namely $\frac{1}{2}$. But it must be emphasized that many more observations would be required to draw safe conclusions from this comparison or from corresponding comparisons worked out for the second column of Table 1 or for the angles listed in either column.

R. F. MILLER,* New Haven, Conn. (written discussion).—In paragraph 4 page 77, Dr. Greninger describes the crystallographic uniformity of the macromosaics, and on page 81 he states that dendrite axes in copper coincide with crystallographic axes. These two statements seem to disagree with paragraph 5, page 77, where he says, "There appears to be little or no connection between dendritic structure and macromosaic structure in copper."

It is difficult to understand how dendrites and macromosaics could be so closely related to the same lattice, and yet not be related to one another. Perhaps if Dr. Greninger would present his evidence for statement 6, this apparent disagreement could be explained.

J. ALEXANDER,† New York, N. Y. (written discussion).—It seems that what Dr. Greninger terms (p. 75) "micromosaic" structure is really *ultramicromosaic* structure. In the ring type X-ray spectrogram a broadening and "fuzzing" of the rings is due to the fact that the crystals are so tiny and numerous that their reflections form a practically continuous ring. Crystals sufficiently small to bring about this result are of ultramicroscopic—that is, colloidal—dimensions. Dr. Greninger's definition of macrograins is sufficiently broad to include true micrograins, and I query whether it would not be better to limit the expression "macrograin" to such as are visible to the naked eye.

In attacking what he terms "the time-honored description of the growth of metal crystals to form polycrystalline aggregates," Dr. Greninger fails to mention that the view he epitomizes as the time-honored one has been attacked before as not all-inclu-

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sive. In view of the evidence brought out in several papers¹⁸, it appears that the course of crystallization very generally passes through the zone of colloidal aggregation, and that this may be reflected in the final structure. The general course of crystallization appears to be: (1) chance aggregation of atoms or molecules into nuclei, which may be crystalline or haphazard clumps; (2) aggregation of these nuclei into spherulites when they grow sufficiently to have a greatly reduced kinetic motion; (3) aggregation of the spherulites into dendritic chains or secondary groups; (4) orientation of these latter into a crystal lattice, usually macroscopic or microscopic, which may show the Smekal-Zwicky secondary structure¹⁹.

A. B. GRENINGER (written discussion).—The author's departure from Tutton's definition of twin formation is in the statement that an initial lattice disturbance is necessary for the formation of a twin nucleus. There can be no doubt that this is true in structures formed by twin gliding, and it seems illogical, in the face of a complete lack of evidence, to exclude the possibility of this happening in the formation of "growth twins," inasmuch as it is certain that lattice disturbances tending to produce departure from exact parallelism are constantly occurring during crystallization. It should be noted that Tutton's definition was made at a time when the ideal crystal lattice was generally assumed to be a reality. According to his statements the formation of a twin would be purely a matter of chance, the molecules in the liquid state evidently being uncontrolled in the choice of forming a complete crystal lattice or of passing to the twin position, even though this latter course would involve a distinct break in the lattice continuity, which in all metal twins except the octahedral type would also involve the introduction of lattice distortion.

A significant observation concerning the Widmanstätten orientation relationships in meteoric irons may be made merely from a visual examination of an etched surface of any of the well developed medium octahedrites, such as the Casas Grandes, Shrewsbury, Coopertown, etc. It can be seen that different sets of kamacite lamellae (that is, lamellae parallel to different faces of the octahedrite structure) will give simultaneous reflections from the etched {100} planes. This observation was evidently first made by Bøggild²⁰, and led to his systematic investigation of the orientation relationships in meteorites. Bøggild examined more than twenty different falls, covering practically all of the well oriented medium and fine octahedrites; the same relationship was found to hold for all of them. Bøggild's findings have been commented upon by Young²¹.

A few salient facts concerning the structure of meteoric irons may be mentioned. First, the structure of the kamacite lamellae in both medium and fine octahedrites always has a certain amount of scatter (deviation from a single-crystal structure), which varies from 10° or 15° for the most well developed octahedrites to complete randomness for others. Of the hundreds of octahedrite falls that have been described, there are only 30 or 40 in which the kamacite can be said to approach (within 20°) single-crystal structure. The structure of the taenite in all cases is much more irregular than that of the kamacite. Taenite seldom, if ever, shows a scatter of less than 20° or 25°, although the octahedrite pattern is usually accurate to within 3° or 4°.

¹⁸ The Colloidal State in Metals and Alloys. First Colloid Symposium *Monograph*, Univ. of Wisconsin (1923).

J. Alexander: *Colloid Chemistry*, 3, 413-438. New York, 1931.

H. A. Endres: in Alexander's *Colloid Chem.*, 1, New York, 1926.

¹⁹ J. Alexander: *Op. cit.*, 13.

²⁰ See footnote 16.

²¹ J. Young: On the Orientation of Kamacite in Meteoric Iron. *Mineralogical Magazine* (1929-1931) 22, 382-385.

In the face of this general imperfection in structure, Young²² reported orientation relationships to within $\frac{1}{4}$ degree, but it is doubtful that his X-ray method for determining orientations could have been capable of such accuracies. The question might be asked: Is it justifiable to assume that the mean positions of the kamacite and taenite orientations, as we see them, are necessarily the same as the kamacite and taenite relations at the time of transformation (if, indeed, there has been any transformation)? Two or three isolated examples might well show approximately the relations found by Young, but it would be necessary to work with a very large number of relationships (as did Bøggild) before the assumption that granulation or scattering has been centrosymmetrical could be justified.

There are many other interesting crystallographic facts concerning meteorite structures, such as the uniform orientation of rhabdites in kamacite, both in the octahedrite and hexahedrite irons. A full discussion of these points properly belongs in a separate paper.

It is generally taken for granted that kamacite (BCC) has precipitated from taenite (FCC); and the broad kamacite lamellae bordered with fine bands of taenite, which constitutes the Widmanstätten pattern, originated in this precipitation or ex-solution. Actually, has this ever been verified? Vogel's lengthy researches²³⁻²⁵ into the metallography of meteoric iron structures and of the corresponding ternary Fe-Ni-P alloys point to an entirely different explanation. Vogel states²⁶ that the broad kamacite lamellae (which he calls W-structure) represent primary crystallization figures. He also gives a metallographic explanation for the other types of meteoric irons, the ataxites and the hexahedrites. Vogel, however, made no attempt to correlate his findings with orientation relationships.

The problem of meteoric iron structures is by no means a solved one. There is need for a thorough investigation, which would combine both metallography and orientation studies and which would attempt to accumulate and correlate the findings of mineralogical, metallurgical, and astronomical studies that have already been made. A few isolated orientation studies cannot hope to alleviate the confusion that evidently exists in this field. In view of the uncertainty of the thermal history of meteorites and the uncertainty as to the origin of the broad kamacite lamellae (although Vogel's explanation is the most attractive), a direct grouping of orientation relationships of meteorites with those of Widmanstätten structures in alloys, such as Barrett and Mehl have made in their discussion, seems unjustified.

The writer is in complete agreement with Barrett and Mehl in their opinion that more data are needed before the theoretical statements contained in the paper may be judged.

Dr. Miller's question might be answered by changing the wording of paragraph 5, page 77, to: "There appears to be no connection between dendrite *boundaries* and macromosaic *boundaries* in copper."

Dr. Alexander has evidently failed to differentiate between the factors that affect Laue patterns (or the diffraction of white X-radiation) and those affecting Debye

²² J. Young: Crystal Structure of Meteoric Iron as Determined by X-rays. *Proc. Roy. Soc.* (1926) **112A**, 630.

²³ R. Vogel: Über die Struktur der Fe-Ni-Meteoriten. *Ztsch. anorg. Chem.* (1925) **142**, 193.

²⁴ R. Vogel: Über die Strukturformen des Meteoreisens. *Abhandl. der Ges. d. Wiss. zu Göttingen, Math.-Phys. Kl.* (1927) **12**, 1-51.

²⁵ R. Vogel: Eine Umfassendere Deutung der Gefügeerscheinungen des Meteoreisens durch das Zustandsdiagramm des ternären Systems Eisen-Nickel-Phosphor. *Ibid.* (1932) **3**, pt. 6, 1-31.

²⁶ R. Vogel: *Ibid.* (1932) **3**, pt. 6, 31.

patterns (or the diffraction of monochromatic X-radiation). Broadening of Debye lines is not due only to small grain size, but also may be due to chemical heterogeneity and internal stresses. So far as the specimen is concerned, the geometrical character of diffraction spots produced on Laue patterns is governed entirely by the orientations of the diffracting planes. Mosaics as large as 0.1 mm. may well produce Laue spot broadening if the orientation differences are slight, while *crystals* of this size (randomly oriented) obviously could not produce broadened Debye rings.

Microscopic Study of Ancient Bronze and Copper

BY C. G. FINK* AND E. P. POLUSHKIN,† MEMBERS A.I.M.E.

(New York Meeting, February, 1936)

A PART of the material incorporated in this paper was derived from the studies of ancient metal objects examined by the authors from time to time for museums and art collectors, in order to verify the age of the metal. The data thus accumulated during several years were systematically surveyed and supplemented by new material obtained in examination of a set of specimens that had been generously donated by museums for this study. Altogether over 50 pieces were investigated, of which 39 are described in this paper. Every specimen is at least 1500 years old; the majority are considerably older. Exact conditions to which these bronze and copper objects were exposed in the ground are unknown, unfortunately. It is safe to say that exposure conditions did not remain constant during the long period of burial. Although the collection of specimens studied represents a wide variation in location and age of the objects, as well as in the nature and composition of the metals, it was found that fundamental changes in the metal structure were limited to a few typical cases which, therefore, may be considered as more or less general. The authors' chief aim was to study the effect of extremely long periods of corrosion on the structure of bronze and copper.

SPECIMENS STUDIED

As the majority of specimens were very small and sometimes had a heavy coat of patina, or crust, which further reduced the amount of metal available for analysis, quantitative chemical analyses were not made. Small detached specimens were not always obtainable and studies had to be made on the statue, or other object, itself. In the description of specimens (Table 1), their approximate compositions determined under the microscope are given. The proportion of tin in bronze containing eutectoid was found by visual estimation of the area occupied by the eutectoid. It was based on the assumption that maximum solubility of tin in copper on moderately slow cooling is 7 to 8 per cent in thin castings and 9 to 10 per cent in heavy castings. When the metal was all

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TABLE 1.—*List of Specimens*

Laboratory No	Illustration	Name of Objects, Their Origin and Age	Nature of Metal
STATUES AND ORNAMENTAL FIGURES			
3	Figs. 1, 19	Chinese statue.	Copper, cast and annealed.
18	Figs. 4, 11-14, 23, 25, 26	Chinese bronze head with two faces.	Cast bronze. Tin 12 to 15 per cent.
5	Fig. 2	Hittite statue of warrior.	Copper, cast and annealed
29		Hittite statue from Metropolitan Museum of Art. Marked 25.96. 2000 B.C.	Cast alpha bronze with small amount of tin.
38		Hittite statue of woman.	Cast bronze. Tin 11 to 13 per cent
17	Fig. 6	Bronze statuette. Location unknown.	Cast bronze. Tin 8 to 9 per cent.
21	Fig. 5	Ornamental figure. Marked 578.	Cast bronze. Tin 8 to 9 per cent.
10		Bronze figure. Marked 10.230.2.	Cast bronze. Tin 11 to 13 per cent.
DAGGERS, SPEARS, HELMETS			
40		Dagger blade from Metropolitan Museum of Art. Early Bronze Age, 3000-2000 B.C.	Wrought alpha bronze with small amount of tin, or impure copper. Forged at low temperature.
41		Dagger blade from Metropolitan Museum of Art. Early Bronze Age, 3000-2000 B.C.	Wrought bronze with small amount of eutectoid. Tin about 8 per cent.
1		Dagger. Excavated in Greece; one of the most ancient bronze objects.	Wrought alpha bronze. Tin probably 2 to 4 per cent.
48		Spear.	Wrought alpha bronze with low tin, or impure copper.
9		Helmet marked 26 54.	Cast bronze with small amount of eutectoid. Tin 7 to 8 per cent
25		Greek helmet from Metropolitan Museum of Art.	Cast alpha bronze forged at low temperature. Tin not over 6 per cent.
MIRRORS			
42	Figs. 9, 10, 24	Hellenistic or Graeco-Roman, 3d century B.C.-4th century A.D. From Metropolitan Museum of Art.	Cast bronze with 18 to 20 per cent of tin and about 10 per cent of lead.
43	Fig. 8	Hellenistic or Graeco-Roman, 3d century B.C.-4th century A.D. From Metropolitan Museum of Art.	Cast bronze with small amount of eutectoid (tin 8 to 9 per cent) and large proportion of lead (30 to 40 per cent).
55	Fig. 22	Etruscan from Fogg Museum.	Cast eutectoid bronze. Tin 25 to 26 per cent.
DISH COVERS AND DISKS			
47		Dish cover.	Cast bronze with trace of eutectoid (tin 7 to 8 per cent) and 30 to 40 per cent of lead.
28		Chinese dish cover marked 77B.	Cast bronze of special composition.
49		Disk.	Cast eutectoid bronze. Tin 25 to 26 per cent.

alpha its tin content could be indicated only within those limits of solubility. In order to distinguish wrought alpha from copper the following observations were considered:

TABLE 1.—(Continued)

Laboratory No.	Illustration	Name of Objects, Their Origin and Age	Nature of Metal
NAILS			
46		Nail from Roman boat raised from bottom of a lake.	Wrought copper.
57		Nuzi Irak nail about 3500 years old. Found in damp clay. Bagdad Expedition.	Wrought copper.
62		Nail similar to 57.	Metal had been entirely mineralized.
69		Nail similar to 57.	Wrought copper.
MISCELLANEOUS			
61	Fig. 3	Nuzi Irak scraper. Marked 28-12.360. Harvard Bagdad Expedition.	Wrought copper cold-worked at edge.
64		Nuzi Irak bronze sheet. Marked 1195. Harvard Bagdad Expedition.	Metal had been entirely mineralized.
67		Hollow cross from China. Marked 116 832(2). Chow dynasty 500 B.C. From Field Museum.	Cast bronze with 11 to 13 per cent tin
70		Egyptian cupped dirk. Marked 30. 437.6. From Field Museum.	Wrought alpha bronze. Tin not over 5 to 6 per cent.
58	Figs. 7, 18,	Etruscan spirals. Marked 24932. From Field Museum.	Wrought alpha bronze. Tin not over 5 to 6 per cent.
6		Egyptian bronze plate.	Cast bronze with 24-26 per cent tin and about 2 per cent lead.
63		Etruscan bronze fragment from Fogg Museum.	Cast bronze with 8 to 9 per cent tin and 10 to 12 per cent lead.
65		Etruscan bronze fragment from Fogg Museum. Dry location.	Wrought alpha bronze. Tin not over 5 to 6 per cent. Lead 2 to 3 per cent.
56	Fig. 21	Etruscan bronze fragment from Fogg Museum.	Cast bronze with trace of eutectoid. Tin 7 to 8 per cent. Lead 1 to 2 per cent.
59		Etruscan bronze fragment from Fogg Museum.	Cast bronze with trace of eutectoid (tin 7 to 8 per cent) and 20 to 25 per cent lead.
60		Etruscan bronze fragment from Fogg Museum.	Wrought alpha bronze with 2 to 3 per cent lead.
66	Fig. 17	Etruscan bronze fragment from Fogg Museum.	Wrought alpha bronze. Lead 2 to 4 per cent.
68		Copper fragment from Kish. 3000 B.C. From Field Museum.	Wrought copper.
50	Fig. 15	Ancient bronze. Location unknown.	Wrought alpha bronze with small amount of tin.
51	Fig. 16	Ancient bronze. Location unknown.	Wrought alpha bronze with small amount of tin.

1. That wrought alpha usually shows a trace of original heterogeneity of the structure, especially after etching with Grard's solution (a trace of dendritic structure visible under low magnification).

2. That in initial oxidation of alpha, metallic copper is deposited, which is not found in oxidation of copper specimens. Sometimes the difference in color was sufficient to make this distinction.

Approximate proportion of lead was estimated by visual integration of its area under the microscope.

POLISHING AND ETCHING OF SPECIMENS

On account of the small size of specimens and especially to preserve the patina at the edge of the sections, all specimens were mounted in fusible metal. The method of polishing was the same as that usually applied in metallography. But when a detached specimen was not available, and polishing had to be done on a small area of the statue or other object itself, an apparatus used for cleaning and drilling teeth was very helpful. It works with small abrasive paper disks and can be used also with polishing powders, so that all stages of polishing from coarse to fine can be carried out on a very small area without mutilating the surface of the object of art as a whole.

For developing the structure of the metal and patina three etching solutions were used: (1) ammonium hydroxide with a few drops of hydrogen peroxide, (2) Grard's solution (ferric chloride in hydrochloric acid), (3) mixture of ammonium persulfate (10 per cent solution) and potassium cyanide (10 per cent solution) in equal portions.

Ammonia etching was applied for exploring the nature of all of the samples as well as for the final development of the structure in copper specimens. Bronze was etched either with ammonia solutions followed by Grard's reagent or directly with a fresh potassium cyanide solution. The latter method is preferable, as it gives very fine differentiation of the structural elements, but in some cases it is not effective.

ILLUMINATION BY DIFFUSE LIGHT

In ordinary metallographic work specimens are illuminated by parallel reflected light. This illumination is excellent for bringing into our vision details of the structure but it fails to convey natural colors of the substance examined. With metals it is not so essential because a majority of their constituents are white or, if colored, their color is well preserved even in regularly reflected light. But with mineral substances it is a different problem. Most of the minerals appear under a microscope either white, light gray or dark gray, though their real color is red, green, etc., consequently they thus lose one of their very important characteristics. Correct disclosure of color is conveyed to us by diffuse light in which a majority of the rays are reflected irregularly; i.e., in all directions. The greater the proportion of such rays in the

beam of light, the brighter will be the natural colors. Daylight is also diffuse but for microscopic examination it is too weak.

It is evident that in examination of the component minerals of patina diffuse light is indispensable. Our method for producing diffuse illumination was quite simple and convenient. A condenser set on the optical bench of the microscope was slightly raised from its normal position and inclined forward, so that the beam of light from the arc lamp passed through it eccentrically. Thus the light was diverted from its regular path, and instead of entering the illuminator it fell on a small concave mirror which had been attached to the arm of the microscope; by mirror it was reflected obliquely on the specimen. The change from the diffuse to regular light, or vice versa, could be made quickly by bringing the condenser from one position into the other. Installation of this kind for operating both types alternately is often very desirable; for instance, in studying the nature of inclusions in metals. As we know, the color of inclusions is one of their important characteristics.

Maximum visual magnification of the colored image was about 500 dia., obtained by combination of 8-mm. objective with eyepiece $\times 20$. With objectives of higher power the distance between the face of the objective and the specimen becomes too short, and the beam of light cannot be directed at a proper angle of incidence.

MICROSTRUCTURE OF ANCIENT COPPER

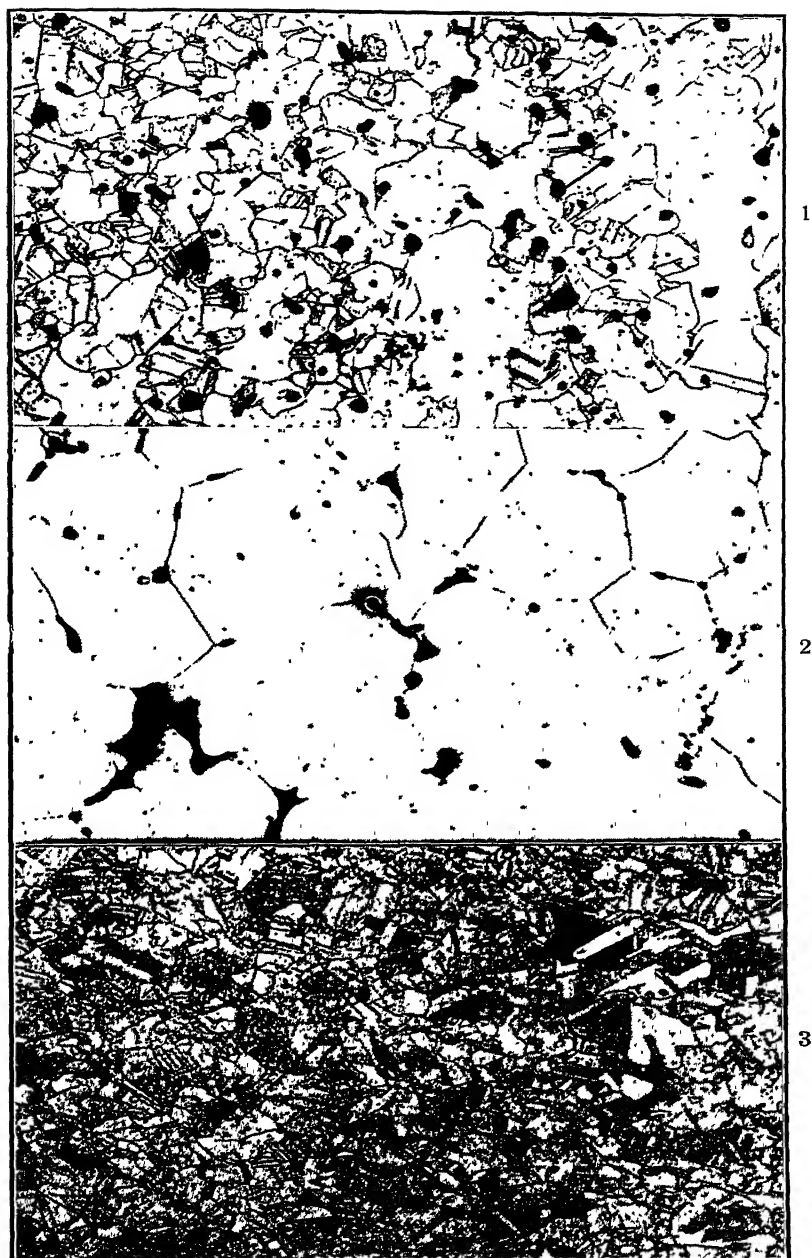
The number of copper specimens was comparatively small; two, Chinese and Hittite statues, were cast and annealed (Figs. 1 and 2). Grains are polygonal and uneven in size but not very large. The Chinese statue contains lead. Both metals have numerous small inclusions of different color, sometimes with duplex structure. Other impurities occur as films on grain boundaries. But the amount of cuprous oxide is surprisingly small considering the age of the metal.

Fig. 3 shows the structure of an ancient scraper from Nuzi Irak. The metal is wrought copper with small polygonal grains, which at the edge of the scraper were distorted by cold-work. Evidently the edge was hammered out cold to make it sharper and harder. This treatment of the cutting edges of tools was common in many ancient countries. Garland and Bannister^{2*}, also F. Giolitti²², mention that its application to knives, axes and razors was common in Egypt, Greece and Rome.

The microstructure of three copper nails, one Roman and two from Nuzi Irak, appeared to be the same as in modern wrought copper, except that the metal was not as clean; likewise, the structure of a very ancient piece of wrought copper from Kish (3000 B.C.) is of this type.

In all specimens examined by the authors the proportion of copper oxide did not differ much from that in standard copper of our own time.

* References are at the end of the paper.



FIGS. 1-3.—ANCIENT COPPER.

1. Specimen 3. $\times 100$.
2. Specimen 5. $\times 200$.
3. Specimen 61. $\times 200$.

It seems that the ancients knew how to protect the liquid metal from oxidation. A substantial difference, however, was found in the amount of other impurities, which were always higher in the old metal. They occurred as inclusions of various colors, or films on the boundaries of grains, and sometimes in solution with copper. When in solution, the presence of impurities could be disclosed by etching. The proportion of lead was not large and in some specimens it could not be found at all. The chemical composition of ancient copper is exemplified by the three following analyses:

Chinese battle-axe heads⁴⁰ (Chow 1122–256 B.C.): Cu, 98.3; Sn, trace; Pb, trace; Fe, 1.7.

Egyptian dagger³: As, 0.39; Pb, trace; Fe, 0.08; copper by difference, 99.53 (oxygen omitted); Bi, Sn, Ni, nil.

Egyptian copper knife³ (Attributed to XVIII dynasty—3500 years old. In a splendid state of preservation.): Pb, 0.63; Fe, 1.18; Bi, 0.44; Sn, 0.03; Ni + Co, 0.26; As, 0.81.

Several investigators² refer to “cored” structure of ancient copper. As this structure is more characteristic for bronze, it will be discussed later.

To sum up the results of the microscopic examination of ancient copper, it is distinguished from the modern metal only by the presence of certain impurities, and, as we shall see later, by microstructural aspects of its initial corrosion.

MICROSTRUCTURE OF ANCIENT BRONZE

The proportion of tin in the bronzes examined varied from 2 to 3 per cent up to 26 per cent, and their structure, therefore, also varied considerably, from low-tin alpha as sole constituent to eutectoid alone. A great majority of the specimens were of cast metal. Fig. 4 represents a typical case. The metal has dendritic structure, which is characteristic for cast solid solutions in general. It consists of inhomogeneous alpha and eutectoid. At the first glance this structure appears normal, and this specimen could easily be taken for the modern bronze, but some of the eutectoid has been stained black (dots in Fig. 4). This staining is well seen under high magnification, as in Fig. 10. The change in the color of eutectoid was caused by infiltration of a corrosive liquid through the bronze and is a sign of a peculiar type of corrosion that is observed in ancient bronzes. In some other specimens corrosion attacked first the alpha constituent, producing rough spots in it. These insignificant appearing marks prove the antiquity of the metal. Another distinctive feature of ancient bronzes is the unusual appearance of eutectoid. In modern bronze it consists of two clearly separated elements, delta and alpha, while in many old bronzes eutectoid is contaminated with some other components (Fig. 5). Contamination of the metal with impurities can easily be explained by the crude methods of making bronze and

the impure raw materials of early epochs. For the same reason, a great majority of the specimens contain numerous inclusions. Tin oxide and copper oxide are found in large quantities. Besides, there are some other inclusions and films that are not present in modern bronze. They vary in color and shape, and sometimes have double contours with the center different in color or in hardness from the periphery (Figs. 6 and 7).



FIGS. 4-5.—ANCIENT BRONZE.
4. Specimen 18. $\times 200$. 5. Specimen 21. $\times 500$.

The proportion of tin in ancient bronzes may be as high as 20 to 25 per cent and sometimes even 30 to 31 per cent. The metal of this type was used in old China for casting mirrors, bells, swords and halberds, arrow heads and also for spoons and water pots³⁹. Roman and Etruscan mirrors were also made of this bronze, as is well illustrated by specimens 42 and 55. It is evident that the high reflecting power of this metal was widely known to the ancient world. Bronze with 25 to 26 per cent tin consists entirely of eutectoid: with further increase of tin, it is a mixture of



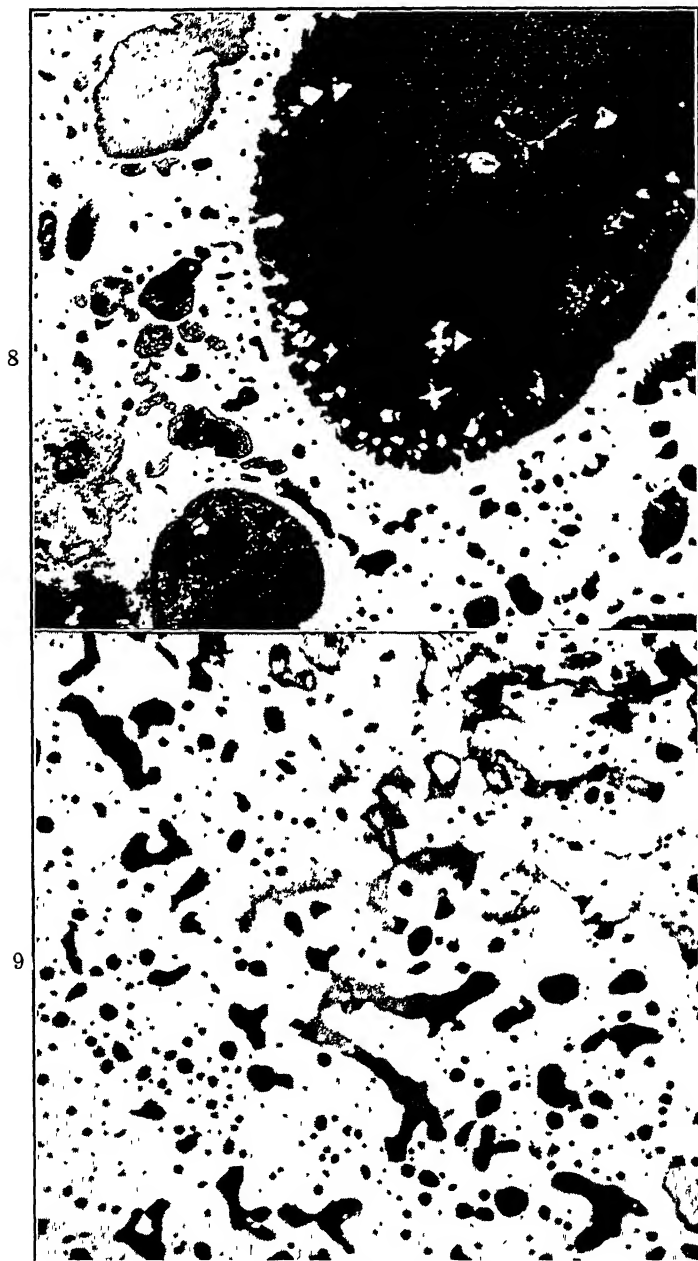
FIGS. 6-7.—ANCIENT BRONZE.
6. Specimen 17. $\times 900$. 7. Specimen 58. $\times 200$.

eutectoid and delta. Both constituents are hard and brittle. Hardness of high-tin bronze was certainly known to the ancients, who used it for making weapons. Moreover, they were familiar with the effect of rapid cooling on the properties of this metal. This statement we base on the examination of mirror 42, which was made of two kinds of bronze. One, forming the back of the mirror, was alpha with a large amount of lead; another, underlying the front face, was mostly eutectoid with a small amount of lead. Examination of the border zone proved that these metals gradually merged into one another, without any distinct demarcation line. It was evident that they had not been fused or welded together, but produced from the same melt. This could be done only by chilling the back of the mirror, so that the first portion of the metal solidified was low in tin while the last portion was highly enriched in this element.

The structure of cast alpha bronze is also dendritic and similar to that shown in Fig. 4, except that eutectoid is not present. Cast solid solution alpha is never homogeneous, but consists of two parts different in composition. Trunk and branches of the dendrites are made of copper-rich alpha, while the space between the branches is filled with tin-rich alpha. This separation of two parts of alpha is very distinct when the metal contains a large proportion of tin. But in low-tin bronze the difference is not striking. The "cored" structure of ancient bronze is nothing else but the ordinary heterogeneous structure of cast alpha. After annealing, it may disappear, if the temperature and time of heating were sufficient to equalize the chemical difference within the metal. When a dendritic pattern is not fully developed, or when it is examined at too high a magnification, it appears under a microscope as a series of black and white areas that are different in hardness and are etched differently. "Cored" structure is also found in copper when this metal contains an impurity in solution.

Several specimens of ancient bronze and copper exhibited a banded structure, caused by forging cast bronze and impure copper at low temperatures; whereby two parts of a solid solution were strung out in parallel bands.

The proportion of lead in ancient bronzes varies within wide limits. Some specimens contain only a trace of it, if any at all, while in Chinese bronze coins current at the time 722 to 481 B.C. lead is 40 to 55 per cent³⁹. In the authors' set of specimens, the highest proportion was, perhaps, 30 to 40 per cent. Fig. 8 shows a typical view of lead globules in mirror No. 43, which has that high percentage of lead. Another view of leaded bronze is given in Fig. 9. Globules displaying gray surfaces were corroded. Sometimes lead occurs in more or less regular crystals. As impurity, lead was probably introduced into the bronze by the impure tin or copper, but when present in large quantities it was undoubtedly purposely added in order to lower the melting point of the metal and



FIGS. 8-9.—ANCIENT BRONZE.
8. Specimen 43. $\times 200$. 9. Specimen 42. $\times 200$.



FIGS. 10-11.—INITIAL CORROSION, CASE I.
10. Specimen 42. $\times 1000$. 11. Specimen 18. $\times 1000$.

improve its casting property. Von Bibra⁵⁴, who analyzed many ancient bronzes, holds the opinion that lead was never found in bronzes of the true Bronze Age, and, consequently, its presence indicates the attainment of a higher stage of culture. M. Busch¹² gives the analysis of an Assyrian bronze with 7.64 per cent lead.

Zinc is also occasionally found in ancient bronze. Gowland⁵⁵ and others maintain that the first occurrence of zinc as an intentional addition to copper dates from Roman time. C. Wang⁴⁴ found that in Chinese bronzes zinc occurs from the first century B.C., but examination of



FIG. 12.—INITIAL CORROSION, CASE I. Specimen 18. $\times 1000$.

ancient records indicated that it had not been recognized as a distinct metal until the 14th century A.D.

INITIAL STAGES OF CORROSION IN ANCIENT BRONZE AND COPPER

In the microscopic study of corrosion of ancient bronze and copper the chief aim of the authors was to examine its initial stage, starting with the first visible changes in the structure of the metal. It was found that these changes vary considerably. If the bronze has two constituents, one may be attacked first, while the other remains unaffected for a long time; or both may be attacked simultaneously. The cause of this selective action should be sought in the nature of the constituents and the corrosive agent. Striking differences were noted also in the path of corrosion. It often followed the boundaries and cleavage planes of grains, as can be expected, but sometimes advanced all over the grains uniformly. In certain objects incipient corrosion penetrated into the grains from their boundaries in concentric zones. According to variations

in the selective action and in the path of corrosion, six typical cases can be distinguished.

Case I. In Cast Bronze.—(1) The first visible change occurs in eutectoid that is stained dark gray or black (Figs. 10 and 11). It is obvious that the staining of eutectoid could be caused only by diffusion of a corrosive agent through it, as no other changes are seen yet.

(2) The next change is observed in copper-rich alpha,* which is decomposed with precipitation of metallic copper (Fig. 12). Tin had been carried away by the corrosive solution.

(3) Metallic copper deposited during the previous stage is oxidized.

(4) Corrosion of tin-rich alpha and also final corrosion of eutectoid take place during stage 3 or later.

This process (case I) reveals two interesting features: (1) that a corrosive liquid will diffuse through a solid substance (the eutectoid) to a considerable depth at ordinary temperature; and (2) that tin-rich alpha is not corroded immediately after the eutectoid has been invaded, though the alpha is in direct contact, but, instead, copper-rich alpha is attacked, which is not in contact with the eutectoid at all. The latter feature would point to the electrolytic nature of corrosion in this case (Fig. 12).

Case II. In Cast Bronze.—(1) In this case, the order of attack is reversed: instead of eutectoid, copper-rich alpha is corroded first, with deposition of metallic copper. Eutectoid, or at least its white constituent delta, remains unaffected (Fig. 13). The resistance of eutectoid to corrosion is so strong that it can be found even in the remote layers of cuprite and malachite, where the rest of the metal has long been mineralized (Fig. 14).

(2) In the next stage metallic copper is oxidized.

(3) Corrosion of tin-rich alpha takes place during stage (2) or later.

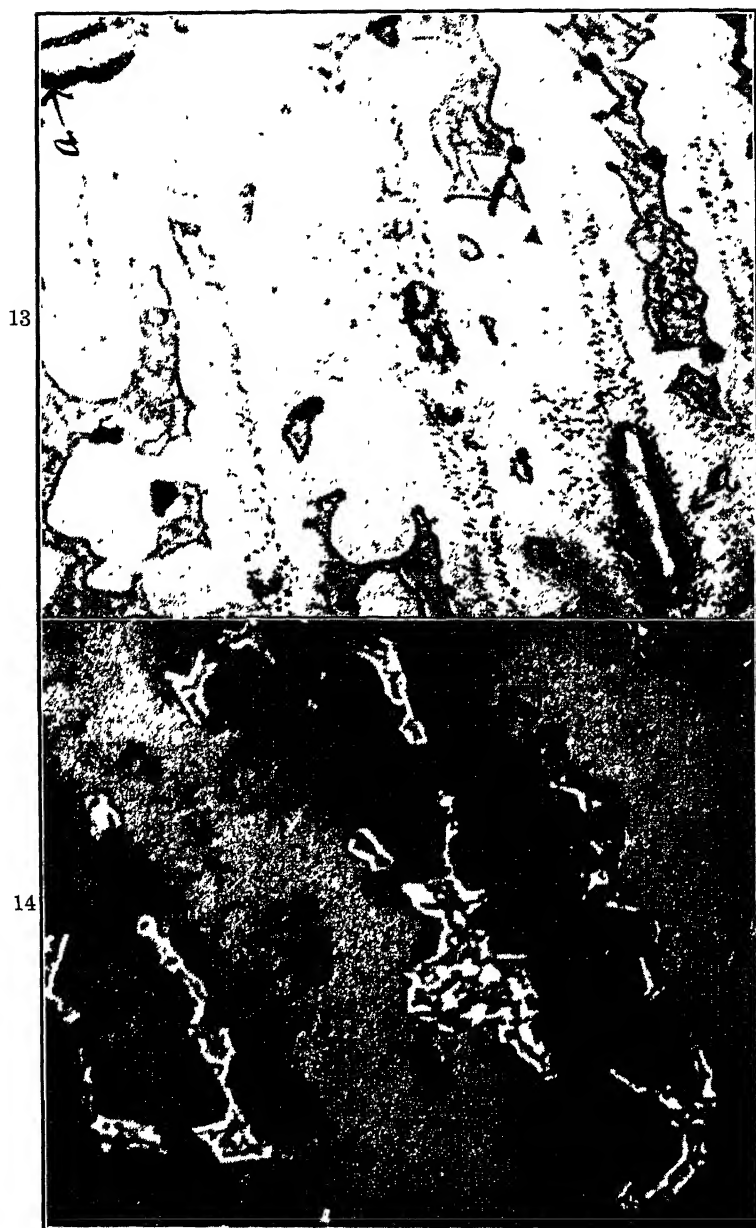
(4) Corrosion of eutectoid is the final stage of the process.

It is interesting to note that both types of corrosion can be found in the same piece. In Chinese bronze 18, for example, a part of the metal was corroded as described in case I, whereas corrosion of some other parts had followed case II. This proves the variations of the conditions surrounding the bronze—possibly different types of corroding solution at different eras.

In the two cases described, corrosion of cast bronze involved both constituents, alpha and eutectoid. Corrosion of a single constituent, alpha or pure copper, either cast or wrought, will now be described. The structural aspects of this corrosion may vary widely, as shown below in four typical cases.

Case III.—The path of corrosion follows grain boundaries and cleavage planes of grains (Figs. 15 and 16). In the first stage alpha is decom-

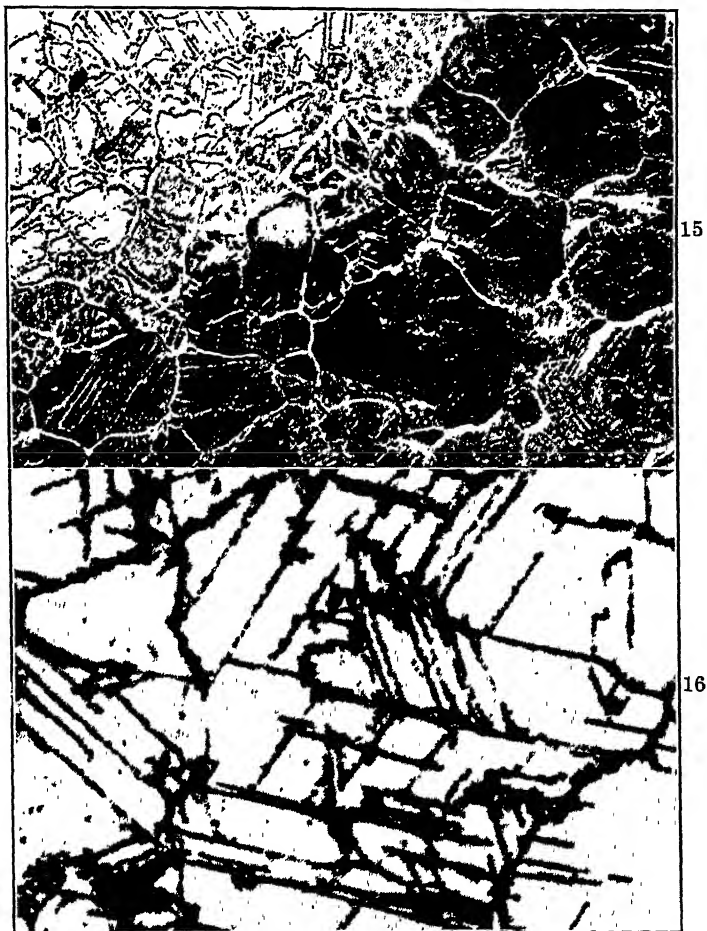
* Cast solid solutions are not homogeneous and exhibit under the microscope two different portions: one is richer in the first element and the other in the second element.



FIGS. 13-14.—INITIAL CORROSION, CASE 11. BOTH SPECIMEN 18. $\times 1000$.
a indicates corroded alpha.

posed with precipitation of metallic copper; in the second, copper is oxidized. In copper specimens there is only one stage marked by the formation of oxide or some other primary product of corrosion along its path.

This type (case III) of corrosion is very common in wrought alpha bronze and wrought copper. It may occur also in cast alpha, but seldom.



FIGS. 15-16.—INITIAL CORROSION, CASE III.
15. Specimen 50. $\times 200$.
16. Specimen 51. $\times 1000$.

Usually the boundaries and cleavage planes were attacked simultaneously, but in some specimens corrosion extended preferably along the boundaries. In bronze 48, for example, cleavage planes were only slightly touched, while the boundaries badly corroded in the entire piece. This preference may be explained by the presence of readily oxidizable impurities on the boundaries of grains. With further progress of corrosion, the number of

corrosion lines within the grains increases and they become wider until the entire area of the grains is oxidized.

Case IV.—Corrosion penetrates into the body of the grains, starting from their boundaries, with uniform speed in all directions, and as a result, the products of corrosion are deposited within the grains in concentric zones. When the first zone is formed at the boundary, the

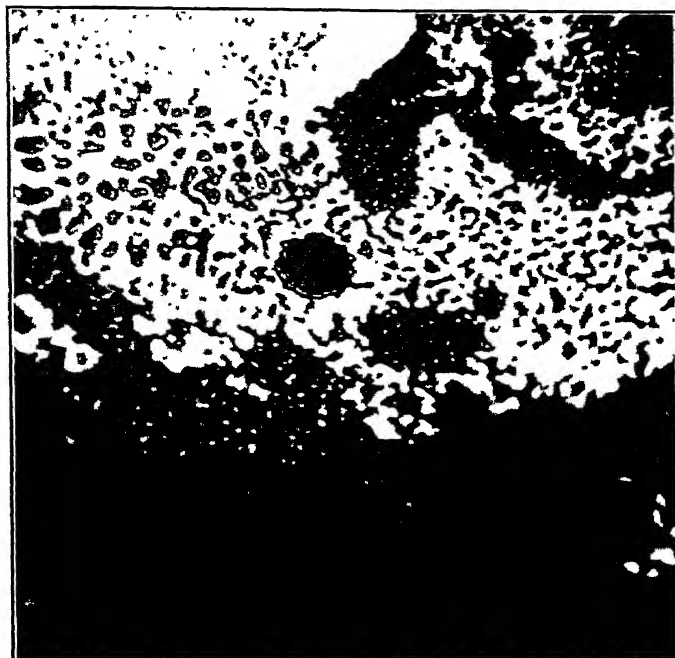


FIGS. 17-18.—INITIAL CORROSION, CASE IV.

17. Specimen 66. $\times 1000$.

18. Specimen 58. $\times 200$.

process continues further and forms the second zone parallel to the first. This goes on until the whole grain is filled with corrosion products (Fig. 17). Near the center of this figure four grains have not been completely mineralized and still show metallic core. In Fig. 18, another specimen is shown with the same type of corrosion. Visualizing this structure in space, we should see that each corroded grain has a nucleus



19



20

FIGS. 19-20.—INITIAL CORROSION, CASE V.
19. Specimen 3. $\times 850$
20. Specimen 58. $\times 1000$.

surrounded by many concentric shells. This type of structure is often found among minerals in crystals of garnet and feldspar. Both specimens of bronze were wrought alpha with small polygonal grains. In the first one, a layer of patina underlying the surface was made of crystalline ruby red patina. Microscopic examination showed that crystals of cuprite had originated from crystals of metal converted into oxide, each one individually, by the process of zonal corrosion described above.



FIG. 21.—INITIAL CORROSION, CASE V.
Specimen 56. $\times 200$.

Patina of the second specimen also has a layer of crystalline cuprite, which in the polished section exhibits polygonal grains with typical pattern of zonal corrosion.

Case V.—Incipient corrosion does not advance in continuous line, like in all previous cases, but starts at many separate points. Minute globules of oxide (or some other primary product) are formed simultaneously at these points. A multitude of these globules embedded in the metal appears like eutectic (Fig. 19). We may call this process dispersed corrosion. The globules increase in size and gradually fill the whole

metal, converting it into oxide. Sometimes formation of globules follows lines parallel to the boundaries of grains. A concentric pattern produced in this case within the grains may be the same as in zonal corrosion, but instead of continuous lines it is formed by dots (Fig. 20). Both types of corrosion, zonal and dispersed, coincide in this case. The question arises why in one metal corrosion extends in continuous lines while in the other it is in separate globules. The underlying cause of the dispersed corrosion lies, probably, in the presence of scattered particles of solid or gaseous impurities, which are oxidized more readily than the pure metal.

Case VI.—The path of corrosion does not follow any specific direction, but advances irregularly (Fig. 21). Neither grain boundaries nor cleavage planes affect the course of corrosion. All grains are gradually merged into a uniform mass of oxidation products. This may be due to an excessively strong corroding agent as compared with those of the other cases above. The difference in speed of attack on the various constituents is relatively small.

MICROSTRUCTURE OF PATINA

Copper and bronze articles taken from the earth or graves are covered with patina, which is a product of chemical reactions between the metal and underground water, air and other chemically active substances. It is very difficult, if possible at all, to visualize the real conditions in the ground where ancient metal has been lying for centuries. Many chemical agencies, such as ammonia and organic acids in the soil, were, perhaps, instrumental in the formation of patina, in addition to carbonated water and air. Electric currents in the ground might have exerted a powerful influence on the course of corrosion. These numerous factors were undoubtedly responsible for the great variety of minerals that were so far identified in patina. Their list includes the following copper compounds:

OXIDES	CARBONATES	SULFIDES	CHLORIDES	SILICATES
Cuprite	Malachite	Covellite	Atacamite	Chrysocolla
Tenorite	Azurite	Chalcocite	Nantokite	
		Bornite		
		Enargite		

Besides, there are lead, tin and iron compounds: cerussite, lead chloride, lead hydroxide, cassiterite, pyrite, markasite, and others.

We must bear in mind also that patination processes have not been always completed, consequently there must be some intermediate products of reactions in patina, such, for instance, as solid solutions.

External appearances and color of patina may vary considerably. Usually it has a more or less rough surface, warty or powdery. But some bronzes have so-called noble patina, which has a smooth, enamel-like surface with all details of the original contours distinctly visible. It is the most desirable type. This noble patina was formed by slow oxidation of dense and homogeneous fine-grained bronzes with smooth surfaces. It

has different colors. Another variety is crystalline patina, in which the outlines of crystals are clearly visible.

The most common color of patina is green, with bluish and grayish tints.

Other ancient bronzes are deep blue, gray, brown or black. Patina of the last three colors is attributed to the presence of lead in bronze. According to our findings, no matter what the intermediate copper product may be—a basic chloride or sulfate—the ultimate product is malachite, a basic carbonate stable in the presence of CO_2 .

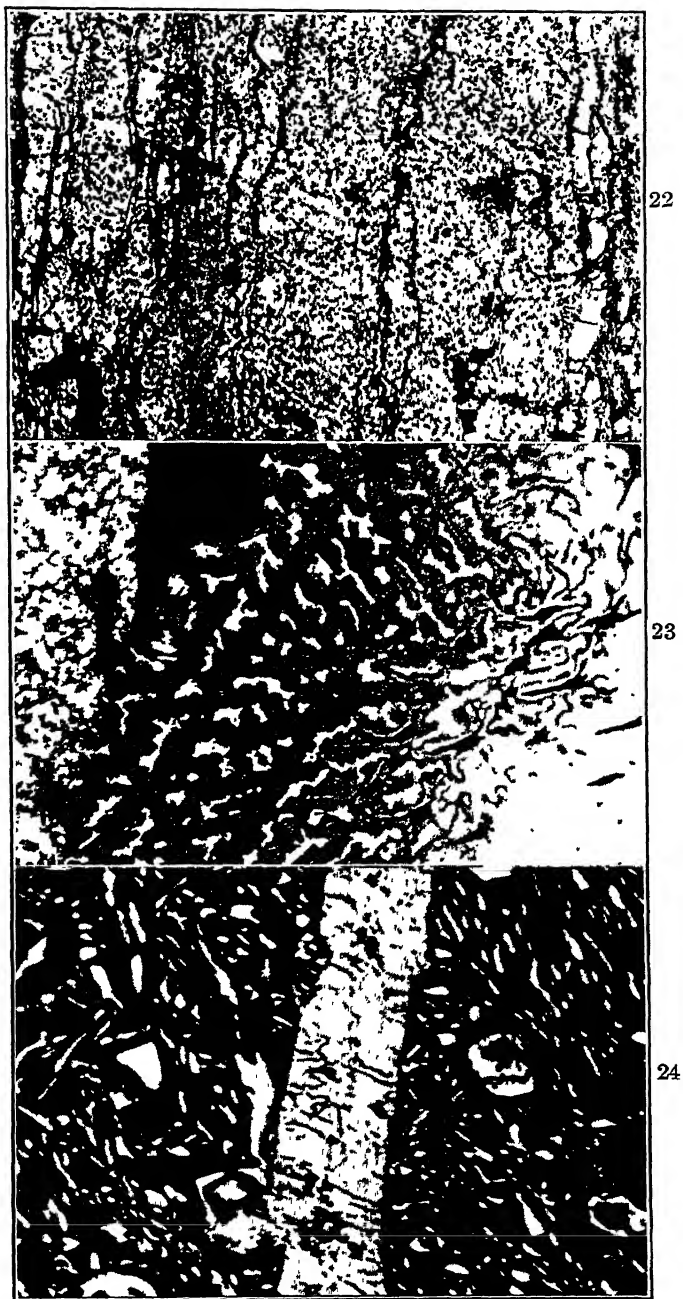
Our study of patina was chiefly concerned with its microstructure. The component minerals were identified visually by examination of their color and structure in both normal and diffuse light. By this method, all common minerals could be identified, but for many others, microchemical tests were needed, which are not yet completed, and for this reason their nature still remains unknown.

Our observation indicated that in all cases where corrosion is merely an oxidation process, resulting only in the formation of oxides and carbonates, the innermost layer of patina is always cuprite, or cuprite and tenorite. Formation of cuprite starts during the initial corrosion. Even in the presence of other corrosive agents such as chlorine, cuprite is frequently found in the first corroded layer in association with other products. Malachite and azurite are never found in direct contact with the original metal.

It should be noted, however, that the term cuprite is not used here in the true mineralogical sense, but in a broader sense to cover all mineral products of patination process in which Cu_2O is a predominant part. It may, for instance, contain tin derived from the corrosion of eutectoid. So long as it displays red color in diffuse light and bluish gray in reflected light, it has been called, conditionally, cuprite. With the same reservation, we use here other terms of minerals found in patina, such as malachite, azurite, etc. No doubt, in many cases they are transitory products of corrosion with varying composition. And, in contrast to true minerals, which also occur in patina, should have specific names.

To show the succession of mineral layers in patina, a few typical cases are given. The component minerals are named in the order of their succession in patina from the metallic core to the outside surface. Unknown constituents are designated by their color in diffuse light (their natural color) and by special letters assigned to each:

- 63. Bronze Cuprite—malachite
- 58. Bronze Impure cuprite—cuprite—malachite
- 64. Bronze Dark gray O—cuprite—malachite
- 65. Bronze Dark yellow-greenish X—cuprite with orange and dark layers—malachite with some azurite



FIGS. 22-24.—PATINA.

22. Specimen 55. $\times 200$.23. Specimen 18. $\times 200$.24. Specimen 42. $\times 1000$.

51. Bronze Impure cuprite—malachite—cuprite
 61. Copper Cuprite—malachite—cuprite—malachite
 62. White T—cuprite—malachite—impure malachite—impure cuprite—malachite

Outside layers in patina generally are older than inside layers, but not always. Mineralization of the metal involves changes in volume and produces fissures which often run parallel to the layers of patina (Fig. 22). Corrosive liquids penetrate into these fissures and deposit metallic copper or cause chemical changes in the adjacent zones of patina. Fig. 23 shows fissures produced along the axes of dendrites in a corroded bronze, and Fig. 24 metallic copper deposited in a crack of stained eutectoid. This copper was brought from other corroded parts of the bronze. Newly formed layers may interfere with the original succession of layers. This explains why sometimes we find cuprite embedded between two layers of malachite, or malachite between two layers of cuprite, as in specimens 61 and 51.

On account of parallel deposition of its component minerals, a patina may have a banded structure. Usually the bands or layers are not numerous and they all follow a certain order, indicating successive stages of patination process. In some specimens, however, the patina shows a large number of various layers without any visible relation to the stages of corrosion. This zonal structure is very characteristic in the patina of ancient Chinese bronze 18. There are 75 different bands or zones in the cross section of this patina, $\frac{1}{4}$ in. thick (Fig. 25). The inner zone, next to the metal, is impure cuprite, the outside zone is malachite. The intermediate zones consist of cuprite and malachite alternating with components of different colors: orange, black, greenish black, greenish gray, yellowish green. In Fig. 25, light bands represent cuprite; dark bands, malachite and all other components. In a part of the cross section all dark bands contain eutectoid (Fig. 26). It is clearly seen in the dark bands adjacent to the metal, but gradually disappears towards the outside surface. Light bands are free from eutectoid throughout the cross section. The presence of eutectoid in the dark bands only and the periodicity of its occurrence suggests that the zonal structure of this patina was probably due to certain periodic heterogeneity of the metal. Further investigation reveals that the original metal had had a very coarse dendritic structure, and that corrosion of parallel axes of dendrites has given rise to white bands, while corrosion of the interaxial portions of metal in which eutectoid was embedded has given rise to dark bands. Fig. 23 demonstrates this origin of zonal structure.

Nevertheless, this explanation cannot be applied in general, as the zonal patina has been found in such metals in which it could not be attributed to the dendritic structure. In these cases another explanation of its origin should be sought. It is probable that this structure was

produced by rhythmical changes in the concentration of corrosive liquids diffusing through the metal. These changes might have been caused by the rotation of seasons. The authors hope to enlarge upon this and other points in a subsequent communication.



FIGS. 25-26.—PATINA.
25. Specimen 18. $\times 100$.
26. Specimen 18. $\times 500$.

SUMMARY

1. In general, the structural peculiarities of ancient bronze and copper are all readily attributable to the crude methods of smelting and treating the metals in the early days of civilization. It is to be noted, however, that the difference between the old and the modern metals is not always very pronounced. There are some examples of ancient metal objects

that are almost free from the usual impurities and their structure is normal in every respect.

2. There is no sign of change in or disintegration of the solid solutions or other components of the metal, except that due to corrosion; this applies even to specimens 5000 or 6000 years old.

3. Microstructural features of initial corrosion and of patina rather than structure of metal give the most reliable proof of the ancient origin of the metal.

4. Our investigations have disclosed characteristic differences in the initial corrosion of the many specimens of widely different origin or location examined. According to variations in the selective action and in the path of corrosion, six typical cases or distinct types of corrosion of copper and bronze were revealed.

ACKNOWLEDGMENT

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DISCUSSION

(Gilbert E. Doan presiding)

C. H. DESCH,* Teddington, Middlesex, England (written discussion).—This paper contains much interesting material, both as to the original structure of ancient bronzes and as to the mode of corrosion. The bibliography will be very useful. The amount of material available to the authors is so large that it would have added value if further particulars could be given. The archaeological data are very scanty; only a few of the specimens are given such particulars as to make it possible to identify their period. The museum number, or the number in the records of an expedition, is not sufficient for the identification of a specimen, and in view of the great difference in composition between specimens from the same site but of different ages, or between specimens of the same age from different sites, the furnishing of exact details is essential.

In the work which I have been carrying out for the Sumerian Committee of the British Association I have found that a complete analysis, including the recognition of small quantities of impurities, is of great value in determining the archaeological importance of a specimen. We have found, for example, that nickel and arsenic are characteristic of certain coppers from Mesopotamia. For instance, the copper ores of Anatolia contain arsenic in fairly large proportion and arsenic is found in objects from Mesopotamian sites just at those periods at which other archaeological evidence indicates that immigration from Anatolia was taking place. On the other hand, specimens from Palestine, which have been examined, are of exceptionally pure copper, and ores of the requisite purity have been found in Arabia. The percentage of tin is naturally interesting, but the proportions of these small quantities of impurities are at least as important. The conclusions of the authors as to the modes of corrosion are interesting, but I would differ from them on one point. On page 110, it is stated that the initial corrosion consists in the formation of cuprite, and that malachite and other minerals are formed by the action of carbon dioxide, etc., on this layer. My own conclusion agrees with that originally put forward by Berthelot, that the primary product is malachite, or some other basic salt if chlorides or sulfates are present, and that the cuprite is formed by a secondary reaction between these minerals and the metallic copper. The process can be imitated artificially, and it is in agreement with the fact that when cuprite is found it is as a layer immediately coating the copper. In some soils in the East there is much chloride, and then the basic salt is atacamite, which is deposited in a similar way.

C. G. FINK AND E. P. POLUSHKIN (written discussion).—We agree with Dr. C. H. Desch that the knowledge of archaeological data is quite indispensable in a study of ancient bronze. A series of specimens, which we examined, had been collected over a period of many years and from various sources. Consequently, the specimen did not represent any definite set of conditions but rather many variations in the conditions of location, burial, age and in the nature of metal. In this heterogeneous material we could very well study such changes in the structural constituents that appeared to be more or less general, and which indicated, therefore, certain trends of corrosion processes.

In regard to the primary products of initial corrosion, we think that the opinion of Berthelot supported by Dr. C. H. Desch is not correct. Our observations have shown that when corrosion is merely an oxidation process resulting in the formation of oxides and carbonates, the first product of corrosion is always cuprite, mixed, perhaps, with tenorite. In these cases, microscopic examination of grains attacked by corrosion has invariably disclosed accumulations of cuprite at the boundaries, or along cleavage

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planes of these grains. If specimens were illuminated with diffuse light, the red color of cuprite was distinctly seen. Generally incipient corrosion of copper-tin alpha starts with decomposition of alpha and, as a result, metallic copper is deposited which is really the first product of corrosion; in the next stage copper is converted into oxide. In the ancient copper specimens the metal is directly converted into cuprite.

If we accept the viewpoint of Berthelot, that the primary product is malachite, we should have found malachite at the boundaries or along cleavage planes of the attacked grains. Its characteristic green color could be readily recognized under diffuse light. But it never occurred as a *primary* product in our specimens of ancient bronze and copper. Of course, we must draw a distinction between the initial stage of corrosion, when the process of corrosion has not absorbed all of the original metal, and the final stage of corrosion, resulting in the formation of massive mineral deposits in the patina. In the course of this latter formation cuprite might be formed as a secondary product, but we have not found any evidence to prove this.

Whenever corrosion products showed the presence of chlorides or sulfates the boundaries and cleavage planes of the grains that were attacked by the initial stage of corrosion appeared gray, brown or black in color. Even in these, red specks of cuprite were often noticeable, but malachite was never found among the primary products of corrosion.

C. S. SMITH,* Waterbury, Conn.—I am extremely pleased to see this paper, and I hope the Institute will have more of a similar type.

Most of the paper is concerned with the corrosion of the alloys, which is a phase about which I intend to say nothing. The authors have attempted to guess the composition of the samples on the basis of the microstructure. This is a rather dangerous procedure, as I have found, to my cost.

Recently I examined some Peruvian bronze objects. The structures were very nice indeed. The metal had recrystallized but still showed distinct coring distorted by cold-working, so I was able to estimate the amount of tin in the alloy and also to describe the probable annealing treatment on that basis. All the analyses I had seen of bronzes from this locality had been either fairly pure copper or copper-tin alloys. A little later I got some more of the same material; enough to have a spectrographic examination and a chemical analysis done. There was not a trace of tin in it. There was 1.5 per cent *arsenic*. Therefore I believe that the use of the microscope alone for estimating composition is unreliable. The combination of the spectrograph and microscope will show composition closely without much harm to the specimens.

On page 99 the authors describe an interesting mirror. The back was of bronze of some composition in the alpha region, while the front contained a much higher amount of tin. I do not believe that the structure they describe would be duplicated by graduated cooling in the manner they suggest. Bronzes do not segregate "normally." They suffer from that peculiar complaint known as inverse segregation, which actually is much more normal than normal segregation.

If the interesting bibliography is a complete one, and contains all the important papers on chemical and metallographic studies of ancient bronzes, it will be of immense value to subsequent students in this field. I should like to make an addition to that bibliography, the recent book by J. R. Partington⁹³. This is an excellent book reviewing and coordinating most of the published material relating to the earliest civilizations. Among other things it contains reference to an analysis of a brass containing 23.4 per cent zinc, at least one thousand years B.C., found in Palestine. This is much earlier than the date for the introduction of brass that is usually attributed to the Romans.

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⁹³ J. R. Partington: *Origins and Development of Applied Chemistry*. London, 1935. Longmans.

C. G. FINK.—First, I want to refer to the slides Dr. Polushkin prepared. These are not hand-colored slides. They are actually colored photographs. So there is no faking of the colors. The colors are there just as they are in nature. Dr. Polushkin deserves a lot of credit for working out the colored slides.

Another point—I certainly want to emphasize the six distinct classes of corrosion. They are really very important from our point of view; that is, when in one the eutectoid is attacked and the alpha is not. In another it is the reverse. The question naturally arises: How can this difference be accounted for? or How can these “annular” rings, like the annular rings of a tree, be accounted for? The only intimation we have is that the acidity or alkalinity of the corroding medium changed with the years, which caused this zonal structure. That is just a theoretical guess or interpretation. But undoubtedly, if we assume that the corroding liquid of one pH will attack alpha, corroding liquid of another pH will attack the eutectoid, we may account for the rings. Even then it is a little difficult to explain because is not the pH going to change during the corroding action? So there really is no satisfactory explanation. That is one reason why no explanation is attempted in the paper.

I am glad to hear the comments by Dr. Smith as far as corrosion goes. The work we present here covers some 14 years, and during that time we have been fortunate in having the assistance of Dr. Lindsley, an expert microchemical analyst. We have also had the cooperation of the Fogg Museum, in particular through Mr. Rutherford J. Gettens. We are not guessing as to the constituents, their chemical analyses having been established definitely within certain limits, and the paper presented is based on the vast amount of information—all of which is not included, naturally.

We have been called upon time and again to decide whether a bronze was made two or three thousand years B.C. or made in Brooklyn last year. Structures such as Dr. Polushkin showed in the slides almost certainly cannot be imitated. It is very easily determined whether a bronze is genuine or not. We have had only one specimen, in all our years of experience, about which we could not decide, and the trouble with that was that the dealer had taken off the outside surface and reached the virgin metal underneath, and that virgin metal was so near in appearance to that of a casting of today that we did not dare even guess whether it was old or new.

J. G. THOMPSON,* Washington, D. C.—Do the synthetic processes that are now in vogue for creating an artificial patina on new copper produce the same structural effects as slow development of the patina by natural processes?

C. G. FINK.—There have been some papers in modern metallurgical journals stating that it is not difficult to analyze the basic carbonate, but that this patina really is a sulfate. It is not carbonate. There are intermediate products, but the ultimate product is malachite. In artificial patination, the usual procedure is to dip the bronze into a solution of ammonium chloride. That gives a beautiful patina, but the chlorides of copper are very unstable in some atmospheres. The ultimate product stable in our climate is the carbonate. Recently we obtained a big sample from Chuquicamata, containing beautiful crystals of brochantite and atacamite, which lasted a very short time in the New York atmosphere. The brochantite is a basic sulfate and the atacamite is a basic chloride.

All the bronzes on exhibition at the Metropolitan Museum are kept in an artificial atmosphere, to preserve both patina and the metal underneath.

In spite of various publications, patina composed of sulfate or of chloride is not permanent. It is true that in the early stages sulfates and chlorides are formed. We have not yet succeeded in artificial patination in developing a crystalline malachite. The natural malachite, basic copper carbonate, is usually crystalline.

* National Bureau of Standards.

Theory of Metallic Crystal Aggregates

By CHARLES G. MAIER,* MEMBER A.I.M.E.

(New York Meeting, February, 1936)

PART I

DENSITY AND ENERGY CHANGES IN COLD-WORKED COPPER

It has long been supposed that when crystalline materials are comminuted the energy used in the production of increasingly smaller grain sizes is not entirely dissipated as heat but that a certain portion is "stored" as a part of the internal energy of the material. This portion usually has been called the "surface energy" of the particles. The practical interest of the Bureau of Mines in this subject in connection with the energy requirements of crushing processes has led to the author's attempt to measure the "stored" energy in finely divided calcite by heat-of-solution methods¹.†

The experiments on calcite showed that "storage" of energy could not be proved for this material, because fine grinding caused a lack of chemical homogeneity evidenced by loss of carbon dioxide and subsequent adsorption of water on the surfaces of the calcite particles. When thermochemical correction was made for composition changes the corrected heat of solution was less for fine material than for coarse. Continuation of the experimental work into the problem of comparing work and heat in the deformation of metallic crystals, where the calorimetric difficulties were less, showed, however, that in the case of copper and aluminum a real discrepancy between work and heat could be shown. Similar results had previously been obtained by Farren and Taylor² and Hort³ and more or less simultaneously with the author's work by Rosenhain and Stott⁴ and by Taylor and Quinney⁵. The results obtained by the different investigators were not satisfactorily consistent, but the experiments of Taylor and Quinney constitute by far the best figures obtained to date.

The previous paper¹ presented evidence to show that if energy is stored in the surfaces of crystals the densities of fine crystals should differ

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† References are at the end of the paper.

from those of coarse particles and gave a formula for calculating such changes. The derivation of the terms of this formula was erroneous, but the qualitative fact remains valid. The present paper proposes to give a more rigorous presentation of the volume-energy relationships and presents a series of experimental measurements of the density of copper undergoing various sorts of cold deformation. The correlation of such theoretical and experimental results, if successful, should be of considerable importance to the theory of metals.

THEORETICAL THERMODYNAMIC RELATIONSHIPS

Using the mnemonic method of Bridgman⁶, one may write the perfectly general thermodynamic equation

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T}{-\left(\frac{\partial V}{\partial P}\right)_T} \quad [1]$$

where E , V , T and P have the usual significance of energy content, volume, absolute temperature and pressure. Further, if α is the coefficient of thermal expansion and β the coefficient of compressibility,

$$V = V_0(1 + \alpha T) \quad \left(\frac{\partial V}{\partial T}\right)_P = V_0\alpha \quad [2]$$

$$V = V_0(1 - \beta P) \quad \left(\frac{\partial V}{\partial P}\right)_T = -V_0\beta \quad [3]$$

Then

$$\left(\frac{\partial E}{\partial V}\right)_T = T\frac{\alpha}{\beta} - P \quad [4]$$

If now the change of volume with pressure in small crystals can be adequately represented by the linear coefficient of compressibility, $-P = \frac{V - V_0}{V_0\beta}$, equation 4 may be written in the differential form and integrated.

$$\int_{E_0}^{E_0 + \Delta E} dE = \int_{V_0}^{V_0 + \Delta V} \left(T\frac{\alpha}{\beta} dV + \frac{V dV}{V_0\beta} - \frac{1}{\beta} dV \right) \quad [5]$$

$$\Delta E = \frac{T\alpha}{\beta} \Delta V + \frac{(V_0 + \Delta V)^2 - V_0^2}{2V_0\beta} - \frac{1}{\beta} \Delta V \quad [6]$$

Further, if ΔV^2 is negligible with respect to $2V_0\Delta V$

$$\Delta E = \frac{T\alpha}{\beta} \Delta V \quad [7]$$

In a similar manner, from the fundamental thermodynamic equation,

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{-V + T\left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial V}{\partial P}\right)_T} \quad [8]$$

With the same assumptions of linear compressibilities and thermal expansiveness the heat-content change becomes

$$\Delta H = \frac{\Delta V}{\beta}(T\alpha - 1) \quad [9]$$

and from

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial V}{\partial P}\right)_T} \quad [10]$$

the entropy change

$$\Delta S = \frac{\alpha}{\beta}\Delta V$$

and finally the free-energy change

$$\Delta F = -\frac{\Delta V}{\beta} \quad [11]$$

Clearly these equations should be applicable to experimentally determined densities for calculating "stored energy," provided that this storage is the result of lattice distortion and that the observed density changes are actually due to it; or, conversely, from measurements of apparent energy storage the expected volume changes may be estimated. The question of the effect of anisotropism (in cubic crystals) will be considered later.

EXPERIMENTAL DENSITY DETERMINATIONS

The proviso that density changes determined experimentally must be actually due to lattice distortion, if thermodynamic comparison with "stored energy" is to be made, implies that the experimental study must attempt to prove whether the changes are produced by strain or are due to a variable "packing density" of mosaic structure. At the beginning of the work the author believed that the comparison of different methods of cold-working, involving variations of stress distribution throughout the samples, might furnish a clue to this factor. The first experiments were performed with this idea in mind. It soon became apparent that

the conditions of annealing were also of considerable importance, and later tests were made to determine the characteristics of the annealing effect. Finally, in order to compare results directly with those of Taylor and Quinney, experiments with torsional cold-working were carried out.

In determining densities, the samples (about 100 grams each) were weighed first in air and later in a light basket of copper and phosphor bronze submerged in carbon tetrachloride. The commercial C.P. carbon tetrachloride of a certain manufacturer was found to have the same density as that given by Timmermans and Martin⁷ for material of highest purity to within three or four parts in 150,000; several batches showed equivalent purity. Although each batch used was checked the material was used without attempt at further purification.

At first weighings by submergence were made, using a Dewar flask as a container for the CCl_4 . The basket was suspended by a 0.003-in. platinum-iridium wire passing through a hole under the pan of a good analytical balance sensitive to 0.0001 gram, the Dewar flask being placed immediately under the balance. With this arrangement it was not practical to maintain a gastight connection between balance and container, although the suspended wire was shielded from air currents by a sectional glass-tubing enclosure. Extremely erratic results were obtained, which were shown to be the result of excessive temperature gradients in the Dewar. A few moments after the stirring of the fluid was discontinued preparatory to making a determination, temperature gradients of 0.5° to 2.0° from the top to bottom of the Dewar were produced, doubtless by the high heat of vaporization of the CCl_4 . Further, it was obviously impossible to stir the contents while the submerged sample was being weighed. These difficulties were largely overcome by replacing the Dewar with a heavy-walled copper container (not thermally insulated from the atmosphere) having a side tube with turbine-type circulating propellor supported by unlubricated ball bearings. This container was nearly filled with CCl_4 ; it had a well fitting cork and a rather small central tube for passage of the suspending wire. Such an arrangement is much superior to the use of an external thermostat.

In making the determination the fluid was stirred for perhaps 5 min. and a weighing made as soon as convection currents had subsided. Two sensitive thermometers (capable of being read to 0.01°C.) were provided at the top and bottom of the container; if they did not give comparable readings immediately after weighing, the observations were rejected.

The weights used were checked against a standard set calibrated by the Bureau of Standards, and appropriate vacuum corrections were made. For further calculation of density two charts were used, one showing the density of carbon tetrachloride at various temperatures from the data of Timmermans and Martin and the other showing the apparent weight

(submerged) of the basket, as determined by direct weighings at a number of temperatures and by further comparison of the relative densities of copper and CCl_4 . The calculations were thus made for the temperature of weighing (submerged) and the densities finally corrected to 20°C . (an intermediate temperature for the observations) by applying a correction for cubic coefficient of expansion based on three times the linear coefficient as determined by Hidnert⁸.

Under favorable circumstances it was possible to obtain comparable "check" readings to within 5 parts per 1,000,000 and consistently to check the density of liquid mercury to within 5 parts per 100,000. This precision is much better than the reproducibility of the density of worked metals that have been subjected to rather severe deformation, and the variations of points in the data from smooth curves are to be ascribed to this latter source rather than to errors of determination.

The actual tests comprising this report are grouped in four sets, as follows:

Group A.—Four samples, of about 100 grams each, of 0.132-in. commercial "soft-drawn" copper wire were annealed at 970°C . in a vacuum of 0.1 mm. for 12 hours.

SAMPLE 1. This sample was drawn through a steel drawplate lubricated with beeswax. A milling machine was improvised as a draw-bench; the feed was 1.5 linear inches per minute. This extremely low rate was used to avoid, if possible, the effects of self-annealing due to internal heating of the wire. After being drawn the samples were washed once in xylol, wiped dry, and then washed five times in carbon tetrachloride, the last time in fresh liquid. The diameter was measured by a micrometer caliper at 4 dia. (45° apart), at the beginning and end of representative pieces, and the eight readings thus obtained were averaged.

SAMPLE 2. The circular cross section (0.132 in.) was hand-rolled to a flat ribbon by newly ground rolls. The cross-sectional area was calculated as the rectangle of dimensions of measured thickness times (measured width—measured thickness) plus the cross section of a circle with diameter equal the measured thickness.

SAMPLE 3. To extend the wire with substantially compressive stresses only, a spiral-rolling machine was improvised. Three small hardened-steel rollers were mounted upon the jaws of a universal lathe chuck in such a way that they pressed uniformly on the periphery of the inserted wire. The ends of rollers were cylindrical, differing 0.002 in. in diameter, and were connected in the center by a short taper; the junction between cone and cylinder was slightly rounded. The reduced end of the wire was clamped into the carriage of the lathe, and a speed of 128 r.p.m. with a feed of 144 was used. The compression of the jaws was adjusted to give a decrease of about 0.002 in. per passage. The rolls and wire were lubricated with a sulfurized oil, such as is used in com-

mercial screw-cutting machines, and the wire was washed after reduction in area in the same manner as in sample 1. With this device reduction in area to nearly 70 per cent could be obtained before the torque of the rolls became sufficient to produce torsional deformation of the wire.

TABLE 1.—*Group A, Samples 1 and 4, Drawn Wires*

Size of Wire, In.	Reduction in Area, Per Cent	Density of Sample 1 at 20° C.	Density of Sample 4 ^a at 20° C.
0 1323	0	8 92426	8 91848
0 1301	3 29	8 92353	
0.1260	9.18	8 92272	
0.1214	15 70	8 92183	8.91640
0.1171	21 59	8 92060	
0.1137	26 13	8 91894	8 91431
0.1109	29 63	8 91742	
0.1068	34 82	8 91414	8 90731
0 1030	39 30	8 91314	
0.1000	42.87	8.91165	8.91116
0.0977	45.48	8.91082	8.91101
0 0902	53 47	8.90877	8 91100
0 0826	60 96	8.90718	8.91124
0.0749	67 90	8.90526	
0.0650	75.84	8.90596	
0.0561	82.00	8.91005	
0.0486	86.50	8 91086	
0.0407	90.53	8.91052	
0.0309	94.53	8.91253	
0.0236	96 81	8 91187	

^a Drawn after twisting 70×.

SAMPLE 4. The wire was twisted cold to a torsional deformation corresponding to $\frac{ND}{L} = 1.25$ (N = number of turns, D = diameter, L = length) and then drawn in the same manner as sample 1.

Group B.—Three new samples of the original wire were annealed at 995°, 1035° and 880° C. in a vacuum of 10⁻⁴ mm. Hg for 12 hr. These samples were drawn as in sample 1, group A.

Two other samples of about 100 grams each were melted in a graphite crucible with tapered sides and a conical bottom. After pumping to a pressure of 10⁻³ mm., the temperature was slowly raised to 1150° C., maintained there for about 1 hr., then slowly dropped to 1050° in about 3 hr. One sample, designated by V , was solidified in the vacuum. The second, after melting and just before cooling, had helium admitted to it at 10 lb. gage pressure. These samples were not drawn or worked. After the upper third of the slug was trimmed to remove any possibility of

cavities about the end of the "pipe" the density was measured. The density of a large single crystal of copper, which previously had been the

TABLE 2.—*Group A, Sample 2, Rolled from Wire to Tape*

Size of Ribbon, In.		Reduction in Area, Per Cent	Density at 20° C.
Thickness	Width		
0 1323	0 1323	0	8 92428
0.1211	0 1342	4.59	8 92394
0.1149	0.1382	4.95	8 92392
0.1088	0.1401	7.57	8 92323
0.1025	0.1413	10.85	8.92287
0.0967	0.1438	13.47	8.92266
0.0908	0 1473	15 51	8.92190
0 0845	0.1518	17.85	8.92167
0 0770	0.1528	23 60	8.92164
0.0710	0.1550	25.88	8.92144
0 0661	0.1575	31.08	8.92041
0 0596	0.1597	36.26	8 91884
0.0530	0.1650	40.70	8 91772
0 0466	0.1690	46.14	8.91610
0.0401	0.1708	52.7	8.91524
0.0343	0.1730	58.6	8.91397
0.0282	0.1770	65.0	8.91490
0.0216	0.1815	72.2	8.91411
0.0155	0.1860	79.4	8.91406
0.0108	0.1890	85.4	8.91531
0.0082	0.1910	88.7	8.91566
0.0060	0.1915	91.6	8.91566
0.0035	0.1940	95.1	8.91423

TABLE 3.—*Group A, Sample 3, Spirally Rolled Wire*

Diameter of Wire, In.	Reduction in Area, Per Cent	Density at 20° C.
0 1323	0	8.92430
0.1312	1 60	8.92417
0.1270	7.78	8.92341
0.1195	18 35	8.92365
0.1140	25 69	8.92416
0.1080	33 31	8 92375
0 1010	41 68	8 92340
0.0950	48.40	8.92261
0.0890	54 71	8 92118
0.0815	62.02	8.91872
0.0750	67.9	8.91581

subject of low-temperature specific-heat measurements¹ in the laboratory of Professor Giaque, of the University of California, was also determined,

Group C.—Two duplicate samples were annealed at 1035° in a vacuum of 10^{-4} mm. Hg. One was drawn as in the tests of group A. The second was drawn until it was reduced about 45 per cent in area, then reduced to 58 per cent with the spiral-rolling device, and then finally drawn again. The purpose of this procedure was to determine whether purely compressive elongation of the wire after considerable drop in density by drawing (corresponding to substantially tensile elongation) would result in appreciable increase in density.

TABLE 4.—*Group B, Samples Annealed at 995°, 1035°, and 880° C.; Drawn*

Size of Wire, In.	Reduction in Area, Per Cent	Densities at 20° C.		
		995°	1035°	880°
0.1323	0	8.92438	8.92763	8.93003
0.1301	3.29	8.92527	8.92861	
0.1260	9.18	8.92525	8.93032	
0.1214	15.70	8.92466	8.93080	8.93566
0.1171	21.59	8.92306	8.93008	
0.1137	26.13	8.92202	8.92959	8.93668
0.1109	29.63	8.92177	8.92866	
0.1068	34.82	8.91880	8.92736	8.93708
0.1030	39.30	8.91643	8.92502	
0.1000	42.87	8.91600	8.92473	
0.0977	45.48	8.91239	8.92264	8.93879
0.0902	53.47	8.90907	8.91806	
0.0826	60.96	8.90687	8.91589	8.94037
0.0749	67.90	8.90355	8.91377	
0.0650	75.84	8.90218	8.91371	8.94062
0.0561	82.00	8.90682	8.91490	
0.0486	86.50	8.90728	8.91644	
0.0407	90.53			8.94217

Group D.—This group consisted of three samples. The first two were intended to be duplicate anneals; actually the annealing temperature of the first averaged 1020° and of the second, 1035° C. The third sample was annealed at 880° C. Each sample consisted of six pieces 7 in. long. They were torsionally cold-worked by clamping the ends in the head-stock chuck and in a fixed chuck on the carriage of a lathe. The rate of torsion was one turn in 40 sec. Successive increments of torsion were used in these tests; at the end of each the residual torsional strain was measured by clamping an indicating needle at the head-stock end, releasing the chuck and measuring the angle of return due to the elastic strain.

RESULTS OF MEASUREMENTS

All of the experimental results obtained are shown graphically in Figs. 1 to 4, each figure corresponding to the items of groups A to D listed

above—group A results being in Fig. 1, etc. It further seems desirable to record certain of the density measurements numerically, as later utilization of the figures might be handicapped if charts only were given. Tables 1 to 4, inclusive, give complete figures for the data of groups A and B, with the exception of the densities of vacuum-melted copper and of the single-crystal copper. At 20° C. the density of copper melted and solidified in vacuum was 8.94153, but when helium pressure was applied

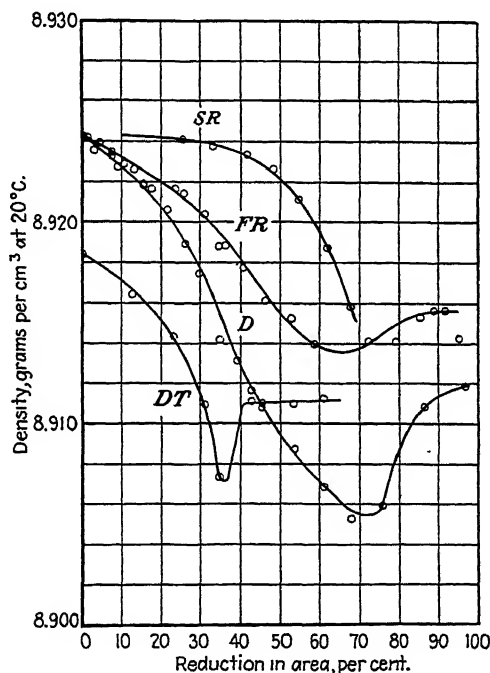


FIG. 1.—DENSITY CHANGES IN COPPER RESULTING FROM DIFFERENT METHODS OF EXTENSION OF WIRE.

Original diameter 0.1323 in.; samples annealed at 970°C., under pressure of 0.1 mm. for 12 hours. *D*, drawn. *FR*, flat-rolled from circular section. *SR*, spirally rolled. *DT*, drawn after torsionally cold-working to $\frac{Nd}{L} = 1.26$.

during the solidification it was 8.94331. The density of the single-crystal sample was 8.95285.

For the group C measurements it does not seem necessary to give all figures, as the variation between duplicates is well illustrated by the chart. The densities at the point of interruption of the drawing and spiral-rolling processes are of interest, however. Thus, at 45.48 per cent reduction the density of the lower curve had dropped to 8.92018; when the area was further reduced to 50.57 per cent by spiral rolling the density increased to 8.92067, but further reduction to 57.71 per cent by the spiral method brought it down to 8.91862. At this point drawing was resumed,

and at 60.96 per cent reduction the density had risen to 8.91886 but thereafter dropped immediately upon further drawing and at 67.90 per cent was 8.91614.

For the sake of comparison the density changes due to spiral rolling only are shown by the upper dotted line in Fig. 3.

The data for torsional cold-working of copper are not tabulated directly but are given indirectly in connection with calculations presented in the next section.

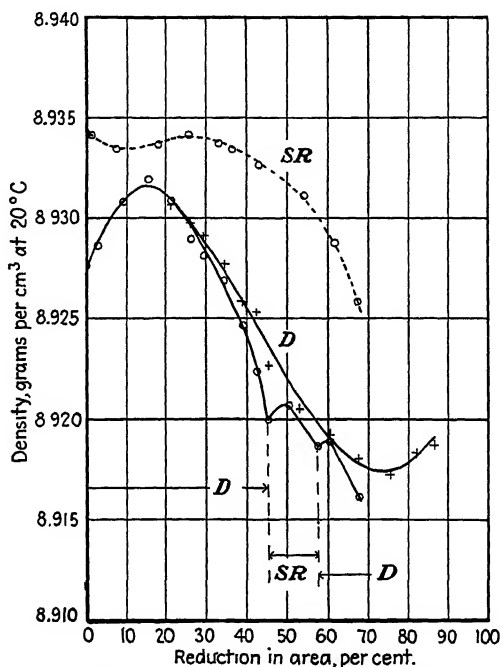


FIG. 2.—EFFECT OF CHANGING METHOD OF REDUCING AREA OF COPPER WIRES.
D, drawn. SR, spirally rolled.

INTERPRETATION OF MEASUREMENTS

Casual inspection of the figures for the density of copper as reviewed by Mellor⁹ or the various values for annealed copper as given above reveals that the density of copper is no very definite figure, even when some information on its treatment, condition and history is given. Leaving out of consideration the effects of impurities, the differences between single-crystal, vacuum-melted or polycrystalline annealed coppers are of considerable magnitude as compared to the effect produced by deformation. The investigator must first attempt to determine how far these changes of density may be attributed to the mosaic structure and how far they may be due to actual fissures, "canals," or other type of pore spaces.

Tammann and Bredemeier¹⁰ have attempted the direct measurement of the "canals" in metals by a method of absorption under pressure of a solution of dye, later to be removed by extraction methods applied to the metal reduced to filings. They found for hard-worked copper 0.6 per cent pore space and for the metal annealed at 900° C., 0.4. For iron containing 0.05 per cent C. they found 0.3 per cent for the hard and 0.6 per cent for the metal annealed at 1000°. However, electrolytic iron drawn from 10 to 0.8 sq. mm. showed: hard, only 0.09 per cent, and

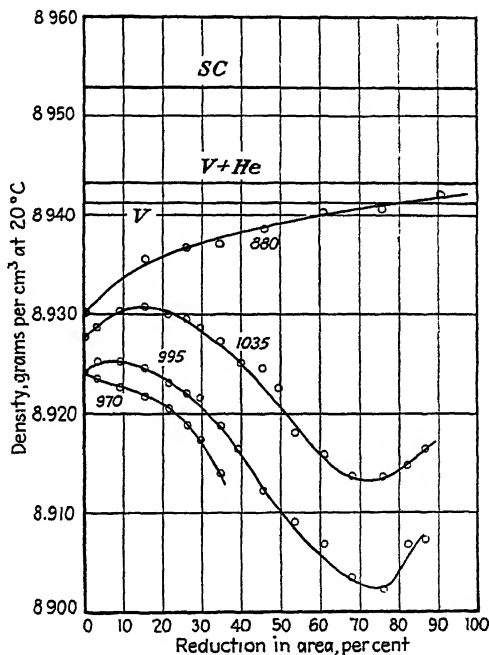


FIG. 3.—DENSITY CHANGES IN COLD-WORKING COPPER ANNEALED AT VARIOUS TEMPERATURES.

SC, density of single crystal of copper. *V + He*, copper melted in vacuum of 0.001 mm. and solidified under 10 lb. helium pressure. *V*, copper melted and solidified in vacuum of 0.001 mm. Figures 970, 995, 1035 and 880 refer to annealing temperatures of various drawn samples.

annealed at 750° C. for 1 hr. in H_2 gas, 0.07 per cent pore space. The reported sensitivity (and accuracy) of the method is stated to be 0.1 per cent. The maximum change of density due to cold-working (by wire-drawing) in the present experiments is slightly less than 0.2 per cent, but the conclusion that the observed changes may be due entirely to opening or closing of the canals does not seem tenable. The samples of copper and low-carbon steel were rolled by Tammann and Bredemeier, but Fig. 1 shows that rolling produces less change of density than drawing. If the smaller density changes due to rolling are a compensation result involving partial closing of the canals by the process, the actual density

changes of the copper itself must have been greater than in drawing. The results of Tammann and Bredemeier with the drawn electrolytic iron wire do not confirm such a hypothesis, because in this case the difference of observed canal space was negligible and the total magnitude within the stated accuracy.

It would naturally be supposed that some information on the maximum density of copper might be derivable from densities calculated from "precise" lattice parameters given by X-ray data. Such measurements were made by Davey¹¹ and more recently by Owen and Yates¹².

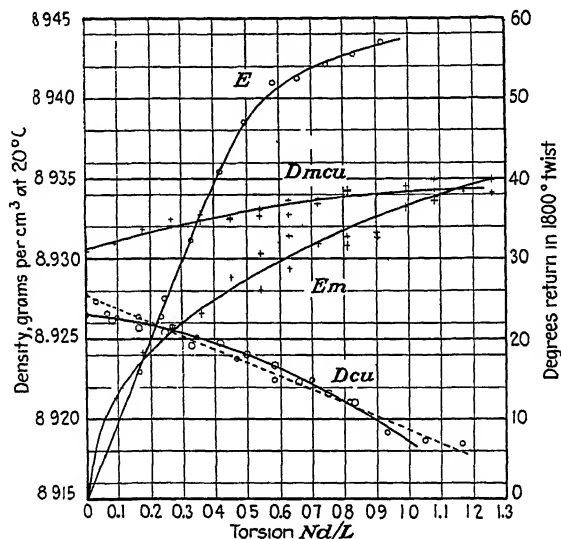


FIG. 4.—DENSITY AND ELASTIC RECOVERY CHANGES RESULTING IN TORSIONALLY COLD-WORKING COPPER.

N , Number of turns of twist. d , diameter. L , length worked (in same units as d). $Dmcu$ and Dcu curves represent density of microcrystalline and macrocrystalline copper, respectively. E and Em curves are elastic recovery in degrees for macrocrystalline and microcrystalline copper, respectively.

For copper the former gives 3.598 \AA. , corresponding to the density 9.002 , whereas the latter finds $3.6077 \pm 0.0002 \text{ \AA.}$ at 18° C. , which calculates to a density of 8.9301 , or 8.9291 at 20° C. The density of the single crystal measured by the author was 8.95285 at 20° , corresponding to a parameter of 3.6032 at 18° , a difference greater than 20 times the stated accuracy of the parameter measurements. The reader will note that the densities of many of the samples measured in the present work were greater than those calculated from the "precision" lattice parameter. Owen and Yates calculated densities from their data and compared them with figures taken from the I.C.T. They attribute the chief error in the density to uncertainty in the mass of the hydrogen atom (or Avogadro's number). Although it is true that the calculated density of copper differs from the

I.C.T. value by about 0.1 per cent, which is also the supposed uncertainty in the mass of the hydrogen atom, it would be expected that the X-ray data should give the density of a single crystal, and for such comparison the discrepancy is definitely greater than the probable uncertainty in Avogadro's number. The author believes, however, that Owen and Yates used too low an annealing temperature (3 hr. at 600° C.) to produce complete recrystallization. There is considerable evidence in the literature to show that severely cold-worked copper does not recrystallize completely at annealing temperatures below 800° to 900°. The data of this report show that between 880° and 970° complete reversal of the density changes on cold-working takes place.

That annealed polycrystalline copper has a lower density than a single crystal and that the difference may be due to the "packing density" of mosaic blocks cannot be denied, nor does the author hold that canals do not exist. The behavior of annealed polycrystalline wire when elongated by nearly purely compressive forces—as, for example, in experiments involving spiral rolling—and the interrupted drawing-rolling processes seem to show conclusively not only that macroscopic pore spaces of the particular samples are not the primary source of density changes in these cases but also that the interstices of mosaic blocks are not *directly* amenable to filling by a squeezing action, and are in fact only in part eliminated by a process of mechanical recrystallization, which will be discussed later.

The most convincing evidence that the density changes measured are related to lattice distortion rather than variations of packing density of mosaic blocks is afforded by a comparison of the magnitude of the density changes observed by the author with measurements of the lattice distortion by X-ray methods on material similarly worked. Such distortion has been investigated by Wood¹³, whose method of calculating latent energy will be discussed later. His actual measurements are not questionable. Wood found for a sample of copper reduced 90 per cent (whether in thickness or area is not stated) that a lattice distortion of $\frac{\delta d}{d} = 16.7 \cdot 10^{-4}$ obtained for approximately $\frac{1}{16}$ of the mass of the sample and $\frac{\delta d}{d} = 2.8 \cdot 10^{-4}$ for the remaining $\frac{15}{16}$ of its mass, where d is the normal spacing determined from the (420) line of copper. Without appreciable error one may take $\frac{\delta V}{V} = 3 \left(\frac{\delta d}{d} \right) = -\frac{D_w - D_a}{D_a}$, where D_w and D_a are the densities of the worked and annealed copper. According to Wood's measurements the density change should be a decrease of $\frac{1}{16}(3 \cdot 16.7 \cdot 10^{-4}) + \frac{15}{16}(3 \cdot 2.8 \cdot 10^{-4}) = 0.110$ per cent.

Table 2 shows that the density of the original sample of rolled copper was 8.92428, at approximately 90 per cent reduction was 8.91566, but at

79.4 per cent reduction in area (which is very close to 90 per cent reduction in thickness) was the minimum, 8.91406. The first of these figures shows a decrease of density of 0.097 per cent, and the second, 0.114 per cent. The concordance of these results with the lattice distortion obviously leaves little doubt as to the source of the *decrease* of density in these measurements.

Other measurements in the literature reveal matters of considerable interest, although the failure of the respective authors to present data from which the mass of material affected could be estimated prevents direct calculation of expected density changes.

Thus, the measurements of Sekito¹⁴ on drawn copper offer a somewhat puzzling comparison with the present work. Sekito determined the effect of heating on the width of Debye-Scherrer lines obtained from cold-drawn copper, and estimates an average internal strain of 0.17 per cent in wire drawn from 2.2 to 0.7 mm. (90 per cent reduction in area) and 0.22 per cent each for reductions to 0.54 and 0.30 mm. (corresponding to 94 and 98 per cent).

By taking the percentage change between the original or maximum and the lowest density obtained (Tables 1 and 4) the following figures are found:

ANNEALING TEMPERATURE	MAX. DENSITY CHANGE, PER CENT
970	0 213
995	0 191
1035	0.259
	<hr/>
	Average 0.22

The change of 0.22 per cent in parameter found by Sekito checks the average density change, but the volume (or density) change that would be expected for Sekito's parameter should be $3 \times 0.22 = 0.66$ per cent. Sekito obtained figures for all three crystallographic planes, and although the figures vary somewhat they are of the same magnitude, and the given results are the average for the three directions. Such a result could be explained if there were expansions in two planes and contractions in the third, corresponding to an average of 0.22 per cent each, but direct proof of such a state is not available from the specific results of Sekito's tests. An alternative explanation of these figures is that the given lattice distortion applied to one-third of the total mass of the material.

Wood's earlier measurements on copper¹⁵ showed that cold-rolling to about 25 per cent reduction in thickness was sufficient to bring the equivalent percentage change in parameter to a constant and limiting value of about 0.33 per cent. Such an increase corresponds to 1 per cent change in density if it referred to the total mass of the sample. The present measurements show that the maximum change in density of copper found between that of a single crystal and the severest lowering

of density by cold-work was never more than 0.6 per cent, which seems to prove conclusively that the measured changes cannot refer to the total mass. In this instance, by reverse calculation, apparently not more than 10 per cent of the metal may be represented as having lattice distortions as measured.

Of further interest in this connection is the fact that Ueda¹⁶ found the maximum change of density in the tensile elongation of copper to be 0.129 per cent, a figure checking in general magnitude with the results found in rolling in the present work.

TABLE 5.—*Torsionally Cold-worked Copper Annealed at 1020°*

$\frac{ND}{L}$	Sp. Vol., C.c. per Gram at 20° C.	$10^4 \Delta V$	$\Delta E = T \frac{\alpha}{\beta} \Delta V$, Cal. per Gram	$\frac{\Delta H}{\Delta V / \beta (T \alpha - 1)}$ Cal. per Gram	$W - H$, Cal. per Gram
0	0.112026	0	0	0	0
0.0833	0.112030	4	0.0019	-0.129	0.026
0.1665	0.112036	10	0.0048	-0.322	0.061
0.2498	0.112038	12	0.0058	-0.386	0.102
0.3330	0.112050	24(?)	0.012	-0.772	0.150
0.4163	0.112047	21	0.010	-0.675	0.212
0.4995	0.112056	30	0.014	-0.965	0.280
0.5825	0.112065	39	0.019	-1.26	0.354
0.6660	0.112077	51	0.025	-1.64	0.436
0.7495	0.112087	61	0.029	-1.97	0.525
0.8325	0.112094	68	0.033	-2.18	0.614
0.9160	0.112096	70	0.034	-2.25	0.701

As the measured density changes have been shown to be consistent with lattice distortion where sufficient data are available to apply the measurements to density calculations, it now becomes justifiable to attempt to calculate energy changes from observed density changes and to compare them with those that have been determined directly. For this purpose the data plotted in Fig. 4 may be used. Tables 5, 6 and 7 show the specific volumes obtained by experiment, calculated values of ΔE and ΔH , and the corresponding values of work minus heat for the same torsional strain as interpolated from the data of Taylor and Quinney.

In calculating ΔE and ΔH formulas 7 and 9, as derived earlier in this paper, were used. The cubic coefficient of copper has been taken from Hidnert as $\alpha = 5.04 \cdot 10^{-5}$, and for the coefficient of compressibility $\beta = 7.43 \cdot 10^{-7}$. Bridgman's figures¹⁷ have been converted to atmosphere units.

Figs. 3 and 4 show that copper may either increase or decrease in density upon cold-working, depending upon the size of crystal (or annealing temperature) and upon the previous cold-work history of the metal. Such experiments as those of Taylor and Quinney cannot be interpreted

generally, because these authors do not show whether the copper they worked was of the type that shows increase or decrease. Their experi-

TABLE 6.—*Torsionally Cold-worked Copper Annealed at 1035°*

$\frac{ND}{L}$	Sp. Vol., C.c. per Gram at 20° C.	$10^4\Delta V$	ΔE	ΔH	$W - H$
0	0.112011		0	0	0
0.0333	0.112015	4	0.0019	-0.129	0.011
0.0666	0.112024	13	0.0063	-0.451	0.021
0.0999	0.112028	17	0.0082	-0.547	0.031
0.1665	0.112027	16	0.0077	-0.515	0.061
0.2331	0.112027	16	0.0077	-0.515	0.093
0.3498	0.112043	32	0.0154	-1.03	0.163
0.4661	0.112060	49	0.0236	-1.58	0.251
0.5825	0.112076	65	0.0313	-2.09	0.354
0.6995	0.112076	65	0.0313	-2.09	0.472
0.8155	0.112094	83	0.0400	-2.67	0.595
0.9320	0.112118	107	0.0515	-3.44	0.719
1.049	0.112124	113	0.0544	-3.64	0.839
1.165	0.112126	115	0.0554	-3.70	0.962

mental work is undoubtedly the best that has yet been reported for the direct measurement of work minus heat. The thermodynamic equations

TABLE 7.—*Torsionally Cold-worked Copper Annealed at 880°*

$\frac{ND}{L}$	Sp. Vol., C.c. per Gram at 20° C.		$10^4\Delta V$, Average	ΔE	ΔH	$W - H$
	Original	Duplicate				
0	0.111973	0.111974	0	0		0
0.0903	0.111969		-4	-0.0019	0.129	0.030
0.1806	0.111959		-14	-0.0067	0.451	0.067
0.2709	0.111951	0.111956	-20	-0.0096	0.645	0.115
0.3612	0.111947	0.111952	-25	-0.0120	0.805	0.171
0.4515	0.111950		-23	-0.0111	0.741	0.241
0.5418	0.111948	0.111944	-27	-0.0130	0.870	0.316
0.6321	0.111936	0.111947	-33	-0.0159	1.06	0.401
0.7224	0.111935	0.111939	-36	-0.0173	1.16	0.496
0.8127	0.111928	0.111929	-45	-0.0216	1.45	0.592
0.9030	0.111930		-43	-0.0207	1.39	0.638
0.9933	0.111924	0.111929	-47	-0.0226	1.51	0.782
1.0836	0.111919	0.111927	-50	-0.0241	1.61	0.876
1.1739		0.111929	-45	-0.0216	1.45	0.968
1.2642		0.111929	-45	-0.0216	1.45	1.045

7 and 9 show that when the specific volume increases (decrease in density), which is the normal behavior for aggregates of relatively large crystals,

the energy content must increase but the heat content must decrease. The change of energy content is obviously negligible compared with observed values of $W - H$, and for this type of change the heat-content change is several times the magnitude of the observed-energy storage and is of the wrong sign. At no time is there any observable relationship between the energy and heat changes calculated from density changes and the measured discrepancies between work and heat. There is little doubt as to the reality of these discrepancies, but it must be concluded that they are not due to lattice distortion.

Wood obtained an approximate check between the maximum energy that was absorbed in Taylor and Quinney's work and that calculated from his lattice-distortion measurements by assuming that the energy-content increase corresponding to the lattice distortion might be calculated as the sensible heat required to raise the temperature to a point of equivalent thermal expansion. This treatment, which neglects the effect of strain completely, does not seem sound, as both the fact of lattice distortion itself and the asymmetric broadening of the X-ray pattern observed by Wood show that a condition of strain existed.

The calculations made from equations 7 and 9 obviously refer to a change at constant temperature; that is, the energy and heat contents of the expanded lattice are compared with the same quantities in the normal lattice at the same temperature; both heat content and energy are intrinsic properties of the material. The calculation made by Wood corresponds to the thermodynamic equation $\left(\frac{\partial H}{\partial V}\right)_P = \frac{C_p}{\left(\frac{\partial T}{\partial V}\right)_P}$. The

correct comparison by this method would entail the following cycle: (1) Expand the normal lattice to the condition corresponding to the distorted lattice, requiring temperature rise ΔT ; (2) remove heat without contraction of the lattice to bring the temperature back to its original condition. The true change of heat content due to lattice distortion only is then $\int \frac{C_{p(N)}}{V_0\alpha} dV - \int \frac{C_{p(D)}}{V_0\alpha} dV$, where C_{p_N} is the specific heat of the normal lattice and $C_{p(D)}$, that of the distorted lattice. It is necessary that $C_{p(D)}$ be greater than $C_{p(N)}$; whence if ΔV is positive more heat must be removed than was added, and ΔH is negative. What Wood did was to compare the heat content of the normal lattice at temperature $T^0 + \Delta T$ with the heat content of the distorted lattice at T^0 , under the assumption that thermal expansion (without strain) could achieve the same physical state. It seems clear that such a comparison has no significance with respect to energy storage.

The general interpretation of the density changes observed with respect to the theory of metallic crystal aggregates will be discussed in Part III.

SUMMARY OF PART I

Density changes in the cold-working of copper may be either positive or negative, depending on the type of cold-working and the conditions of annealing.

The observed density changes have been partly interpreted in terms of lattice distortion, and the basis for attempting to calculate changes-of-energy content from changes of specific volume have been given.

Changes of energy and heat content due to lattice distortion have been calculated from fundamental thermodynamic equations and shown to be inconsistent with directly determined "stored" energy in torsional cold-working.

PART II

DENSITY, COERCIVE FORCE AND ENERGY CHANGES IN COLD-WORKED IRON

In discussing the interpretation of the complex variations of density with cold-working of copper described in the preceding paper¹, Mr. R. S. Dean made the fruitful suggestion that the relationship between coercive force and density changes in the cold-working of pure iron might throw light upon the nature of physical changes taking place. Recent studies of the metallurgical division of the Bureau of Mines¹⁸⁻²⁰ have shown that the coercive force for magnetite powders, as well as a considerable portion of the data on the effect of grain size on the magnetization of metals, indicates a linear relationship between coercive force and specific surface of the particles or grains. As the coercive force during cold-working of pure iron may change several fold in magnitude its measurement constitutes a very sensitive method of investigating the effect of cold-work and, according to this theory, an easy means of determining the change of internal crystal surfaces for those magnetic materials of sufficient purity to eliminate the possible disturbing effect of constitutional inhomogeneities.

EXPERIMENTS PERFORMED

In the present experiments Armco-iron welding rods 0.1875 in. in diameter were used as samples. According to the manufacturer, the material contained 0.01 per cent C and 0.02 per cent Mn, and was not further analyzed. The samples were annealed at various rather high temperatures in a high vacuum, and small amounts of sublimed materials were always found in the colder parts of the clear silica tubing used as container. The sublimate contained carbon, manganese and silicon, indicating that the annealed samples had been purified still further by the vacuum treatment.

The samples were divided into two groups: Group A, consisting of three samples, was annealed at 720°, 910° and 1005°, respectively, in a vacuum of 10^{-5} , 4.10^{-4} , and 10^{-3} mm., respectively. They were maintained at these temperatures for 12 hr. and slowly cooled through the β range in 12 hr. Torsional cold work was done in the same manner as for the copper samples in Part I, measurements being made of density, coercive force and residual torsional strain. Coercive force was measured according to the method suggested by Steinhaus²¹ for materials of low coercive force. Samples 7 in. long were clamped axially in the center of a long solenoid containing a small inner search coil, which could be withdrawn from the sample by the action of a phosphor-bronze spring. The axis of the coil was perpendicular to the horizontal component of the earth's field. A ballistic galvanometer of moderate sensitivity was capable of detecting a variation of reverse field of approximately 0.001 gilberts per centimeter. The measurements on a single sample were reproducible to about 0.5 per cent, but the variations resulting from ununiformity of annealing, structure or cold-working were at times as high as 1.5 to 2 per cent.

Thus, the ends of the specimens, which had not been twisted but had been clamped in the jaws of chucks used to apply the torsion, caused erratic magnetic and density results in the first samples annealed at 720°. Later samples were cut with a thin abrasive wheel just within the twisted portion before measurement. It was found also that the application of successive increments of torsion between measurements did not give results as consistent as when a number of samples were twisted to various degrees of $\frac{Nd}{L}$ uninterruptedly from the annealed state, and this procedure was adopted in the second and third test.

Group B consisted of a single sample annealed at 1026° C. for 12 hr. in a vacuum of 10^{-3} mm. It was drawn in the same manner as the copper samples in Part I. Measurements were made of diameter, density and coercive force. To avoid loss of sensitivity as the wires became smaller in diameter, bundles of the finer sizes were bound together with silk thread, each bundle of wires having approximately the same total cross section as the original sample. An experiment with wires of intermediate size, using one, two and three wires in the magnetic apparatus, showed that within the normal experimental error the same coercive force was obtained, although the sensitivity was necessarily less for the smaller amounts of iron within the search coil.

In all of the measurements the field was brought to 200 ± 2 gilberts per cm. each time before a measurement was made. Although it was possible to calculate $\mu = \frac{\Delta\beta}{\Delta H}$ for the part of the magnetization curve near $B = 0$, $H = H_c$, the method used is not entirely satisfactory for

permeability or for determining the magnetization curve. The values so obtained were near 500 to 600 but, as the initial permeability of iron does not change markedly with cold-working and as the method was unsuited for this purpose, no attempt was made to determine the complete magnetization curve.

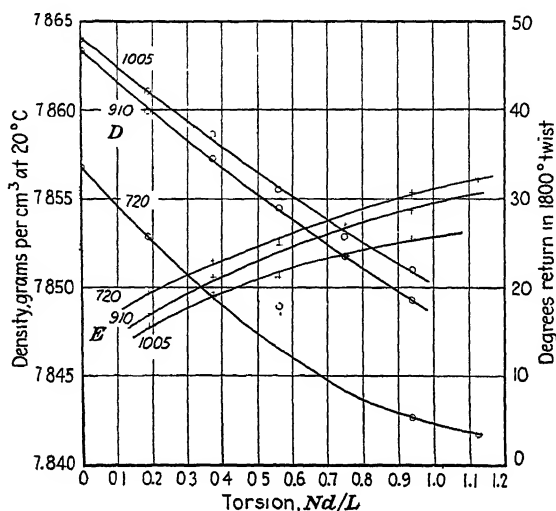


FIG. 5.—DENSITY AND ELASTIC RECOVERY CHANGES IN TORSIONALLY COLD-WORKING ARMCO IRON.

D, density curves. Numerals 720, 910, 1005 refer to annealing temperatures. *E*, elastic recovery curves, numerals as above.

EXPERIMENTAL RESULTS

Tables 8 to 10 record the results of the measurements on torsionally cold-worked iron and Table 11, those for the drawing of the same material. Fig. 5 shows graphically the variation of density and residual elastic strain for the torsional tests and Fig. 6, the density plotted against coercive force. In Fig. 7 the variations of density and coercive force

TABLE 8.—*Torsionally Cold-worked Iron Annealed at 720° C.*

$\frac{ND}{L}$	Density, Grams per C.c. at 20°	Coercive Force, Gilberts per Cm.	Residual Elastic Strain, Degrees Return
0	7.85678	1.709	
0 1875	7.85286	3.861	19.5
0 375	7.84968	4.898	23.0
0.5625	7.84898	6.44	25.4
0 9375 (1st)	7.84491	8.02	30.7
0 9375 (2nd)	7.84262	8.34	30.4
1.1250	7.84176	9.77	32.2

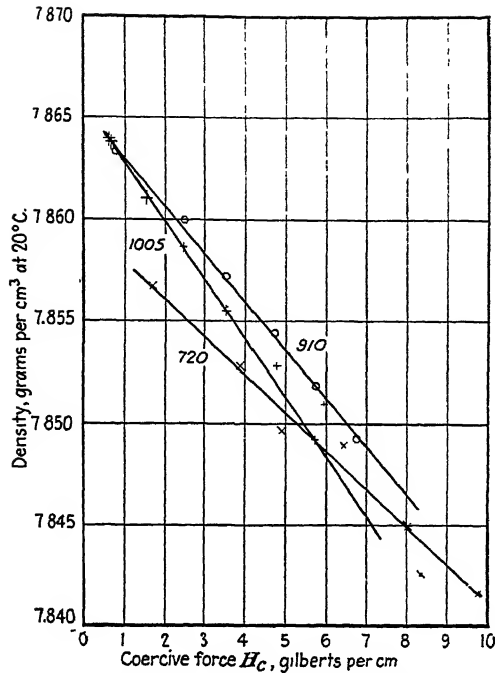


FIG. 6.—COERCIVE FORCE AND DENSITY CHANGES IN TORSIONALLY COLD-WORKED IRON. Numerals refer to annealing temperatures of respective samples

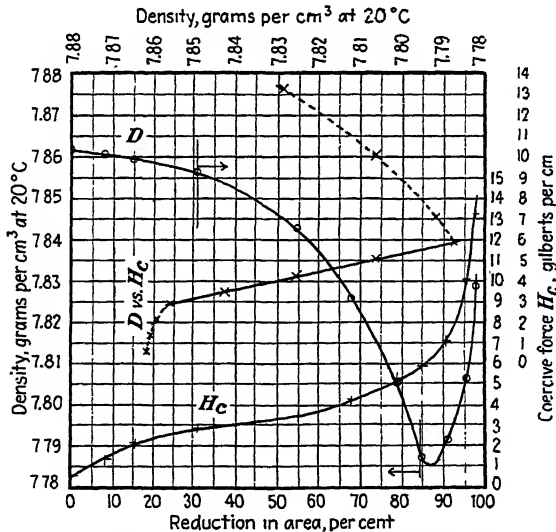


FIG. 7.—DENSITY AND COERCIVE-FORCE CHANGES IN DRAWING ARMCO IRON WIRE. D curve shows variation of density plotted against reduction in area. H_c curve shows variation of coercive force with reduction in area. D vs. H_c curve has ordinates at top of diagram, and abscissas at right. Field of linear relationship between D and H_c , shown by full line, is also shown by arrows and cross lines on D curve.

are shown on the D and H_c curves and upon the alternate set of coordinates, the relationship between density and coercive force.

TABLE 9.—*Torsionally Cold-worked Iron Annealed at 910° C.*

$\frac{ND}{L}$	Density, Grams per C.c. at 20°	Coercive Force, Gilberts per Cm.	Residual Elastic Strain, Degrees Return
0	7.86333	0.789	
0 1875	7.85995	2 506	17.0
0.375	7.85726	3.540	21.1
0.5625	7.85444	4 710	24.8
0.750	7.85183	5.755	27.0
0 9375	7.84921	6 745	28.7

TABLE 10.—*Torsionally Cold-worked Iron Annealed at 1005° C.*

$\frac{ND}{L}$	Density, Grams per C.c. at 20°	Coercive Force, Gilberts per Cm.	Residual Elastic Strain, Degrees Return
0 (1st)	7.86397	0.641	
0 (2nd)	7.86389	0.682	
0.1875	7.86105	1.566	15.6
0.375	7.85868	2.484	19.1
0.5625	7.85554	3.515	21.1
0.750	7.85286	4 760	23.5
0.9375 (1st)	7.85097	5.965	25.5
0.9375 (2nd)	7.84926	5.710	

TABLE 11.—*Drawing Iron Annealed at 1026° C.*

Average Dia. of Wire, In.	Density, Grams per C.c. at 20° C.	Coercive Force, Gilberts per Cm.	Reduction in Area, Per Cent
0.1875	7.86158	0.544	0
0.1797	7.86068	1.391	8 2
0.1726	7.85919	2.127	15.3
0.1562	7.85649	2.876	30.6
0.1262	7.84288	3.472	54 7
0.1068	7.82576	4.240	67 6
0.0862	7.80614	5.050	78 9
0 0730	7.78731	5.885	84 8
0 0565	7.79157	7.105	90.9
0.0395	7.80643	10 07	95.6
0 0263	7.82865	13 25	98 0

INTERPRETATION OF RESULTS

The similarity of shape of the curves showing the variation of densities with torsion and drawing, illustrated in Figs. 5 and 7, with homologous

curves for normal macrocrystalline copper, is striking. So far as the author is aware, the minimum in the density of drawn iron has not previously been described in technical literature, although well known for copper^{22,23}. The chief difference in the curves for drawn copper and iron wires is the considerably greater change between the original density and that at the minimum for the latter, approximately 0.2 per cent for Cu and 1 per cent for Fe. The subsequent recovery beyond the minimum is correspondingly greater for iron, but the position of the minimum is farther along on the percentage of reduction axis. In Part III the general interpretation of the shape of these curves will be discussed in more detail. The relationship of coercive force to density is of greater immediate interest.

Fig. 6 shows an almost exactly linear relation between the density and coercive force of torsionally worked iron, especially in the samples annealed at 910° and 1005° C., of which the untwisted ends were removed before measurements were taken, and on which the results were more concordant. The experiments performed before the measurements on drawn wires seemed immediately to confirm the idea that the change of density is caused by the formation of new internal crystal surfaces. In the drawing experiments, the fact that the curve for density vs. reduction in area shows a minimum, while the coercive force continually increases, precludes any completely linear relationship between coercive force and density. The D vs. H_c curve of Fig. 7 reveals that five intermediate points, shown as a full line, exhibit the linear quality over a part of the drawing range. The dotted curves at the two ends seem to meet the full line more or less discontinuously, especially for the last portion of the data, but the original curves from which the data are taken, with change in area as the independent variable, do not show breaks or any real evidence for discontinuity—the D vs. H_c curve is simply three lines approaching most closely to the experimental points.

The straight lines shown for torsional cold-working in Fig. 6 offer opportunity to extrapolate to zero coercive force and would show an intercept at $d = 7.866$, presumably the density of a single crystal. The idea that the coercive force of a single crystal of pure iron approaches zero has been advanced by Gerlach²⁴. However, attempts to extend the data to points above those shown at the top of the lines of Fig. 6 failed to realize experimentally the further approach to zero coercive force. Thus, a series of 24-hr. annealings at temperatures of 910° to 1025° resulted in measured values for density and coercive force that fluctuated about the upper point with variations no greater than the experimental error. As all of these anneals were made in the region of γ iron, and as a considerable volume change occurs at the transition from γ to β iron, the residual coercive force upon repeated annealing may be ascribed to internal crystal surfaces produced by the volume

change through the transition. Further, *complete* recrystallization can be obtained only with difficulty if at all below the transition temperature, which might indicate that zero coercive force and true single-crystal structure could be realized only by crystals of iron produced below the transition temperature.

The first part of the D vs. H_c curve for drawn wire may perhaps be explained as an effect due to a residue of the changes occurring in passing through the transition.

The data of Taylor and Quinney⁵ for decarburized mild steel do not extend to values of Nd/L greater than about one-half of the total torsional strain applied in the present experiments. In so far as their figures go, Table 12 compares their results with calculated energy and heat-content changes obtained from volume changes and the thermodynamic formulas 7 and 9 of Part I. Here, again, as for copper, there does not appear to be any relation between the measured difference of work and heat and thermodynamically derived figures for energy or heat-content change.

SUMMARY OF PART II

The variation of density of iron with cold-working by torsion or drawing is similar to the changes observed in copper, including the presence of a minimum of density observed in the drawing process.

In torsionally cold-worked iron the coercive force and density show a linear relationship attributable to the formation of internal crystal surfaces.

In cold-working by drawing, a linear relationship is observed over only part of the density and coercive-force changes.

Energy and heat-content changes calculated from measured-volume changes by fundamental thermodynamic relationship indicate that the "storage" of energy in cold-working cannot be ascribed to lattice-distortion energy.

TABLE 12.—*Calculated and Observed Energy Changes in Torsionally Cold-worked Iron*

Anneal	$\frac{ND}{L}$	Sp. Vol., C.c. per Gram at 20° C.	$10^6 \Delta V$	ΔE (cal.)	ΔH (cal.)	$W - H$ (cal.)
910	0	0.127172	0	0	0	0
	0.1875	0.127227	55	0.024	-2.21	+0.216
	0.375	0.127270	98	0.043	-3.93	+0.486
	0.5625	0.127316	144	0.063	-5.77	0.643
1005	0	0.127162	0	0	0	0
	0.1875	0.127209	47	0.021	-1.89	+0.216
	0.375	0.127247	85	0.037	-3.40	0.486
	0.5625	0.127298	136	0.060	-5.45	0.643

PART III

APPLICATIONS OF EXPERIMENTAL WORK TO A GENERAL THEORY OF METALLIC CRYSTAL AGGREGATES

The reader of Parts I and II may have been impressed by an apparent inconsistency: A conclusion of the experiments on copper was that the density changes observed were essentially consistent with lattice distortion as revealed by X-ray methods, but in the experiments on iron a similar effect was ascribed to the formation of internal crystal surfaces. Both of these explanations can be true only if lattice distortion is the *result* rather than the *cause* of the physical changes taking place upon cold-working of metals.

The effects ascribed to lattice distortion are so well attested by a great mass of experimental results, especially those of X-ray studies, that it is not strange to find one school of metallurgists explaining the work and alloy-hardening of metals as due entirely to lattice distortion. A truly satisfactory hypothesis nevertheless must offer adequate explanation not only of density changes and changes of hardness but also of the effects produced by energy changes. Parts I and II have shown that observed energy changes are utterly inconsistent with the required thermodynamic results of the volume changes attendant upon lattice distortion.

Much that has been written concerning lattice distortion seems to imply continued homogeneity in the material after deformation, but the evidence of X-rays interpreted as lattice distortion is also the strongest evidence of lack of physical homogeneity. It is not necessary to itemize here the results of individual experiments, as an excellent and impartial review has been given by Elam²⁵. The question here is not the uniform distortion below the elastic limit, but, as stated by Elam, "as soon as the elastic limit is exceeded the character of the X-ray reflections changes entirely," yet "the earliest investigators of severely worked metal wires and foils showed there was no difference in the spacings of the lines obtained from powder photographs," leading "to the conclusion that, whatever the distortion in the region of the slip planes, there are relatively large layers or blocks of crystalline matter which are unaffected by the general deformation, except to a degree comparable with elastic distortion." Thus, for example, Wood¹³, in calculating the results of his measurements on lattice distortion, found it necessary to assign one degree of distortion $\frac{\delta d}{d} = 2.8 \cdot 10^{-4}$ to $15/16$ of the material, whereas the remainder was estimated at $\frac{\delta d}{d} = 16.7 \cdot 10^{-4}$. Further, Jeffries²⁶ was unable to detect work-hardening in aluminum and aluminum-copper

alloys owing to a condition that must have involved largely isotropic lattice distortion. If this is accepted, the proponents of the lattice-distortion theory of hardening must either attribute the change of physical properties observed in the deformation of pure metals to anisotropic lattice parameter changes or else admit that the lattice distortion observed may be the result rather than the cause of the processes that accomplish not only hardening but also changes of other physical properties of the material, such as density, magnetization, etc.

If a deformed metal can no longer be considered physically homogeneous the assumption that it may exist as a two-phase system is the simplest one in an attempt to analyze quantitatively the phenomena observed. To do so is not necessarily strict subscription to the amorphous cement theory of Beilby, Desch, and Rosenhain. In discussing the slip-interference theory of Jeffries and Archer²⁷, Merica²⁸ makes the following comment:

I have preferred to ascribe the slip interference to atomic forces acting at the surface of the key particle and through one or more atomic layers of the surrounding matrix. Thus one can regard the particle as in a sense adsorbing the surrounding medium or solvent and surrounding itself with a film whose properties are markedly different than in the undisturbed atomic matrix of metal.

So also Dean and Gregg²⁹ state that:

the existence of these intercrystalline boundaries has a considerable effect on hardness is well known. Recently Angus and Summers³⁰ have shown that for copper the relation between hardness and crystal surface is a linear one. If we know, then, the structure of these crystal boundaries we should have a very good start toward a general theory of hardening.

TENTATIVE HYPOTHESIS

As a working hypothesis, the assumption that deformed metals consist of two phases, one of which is the normal lattice with lattice distortions comparable to the elastic-limit deformation and a second existing at internal crystal surfaces, will be made. For the present the nature of the second phase, which for convenience in reference the author has termed¹ the " ω phase," need not be specified. Rather, certain properties will be ascribed to the ω phase and the resulting implications examined in comparison with observed behavior.

One such set of properties has been postulated by Dean and Gregg in the article cited:

Now from the metallic structure we have developed, it is obvious that at a discontinuity in the lattice a special set of conditions must prevail. The atoms are further apart than in the normal space lattice; that there is no actual discontinuity, however, is shown by the great strength of these boundaries and by the conduction of the electric current across them.

If the atoms at the grain boundaries or in internal crystal zones are farther apart, the density of the ω phase is less. Although metals can be plastically deformed, nevertheless they do not show true fluidity; whence in maintaining its dimensional rigidity the formation of a quantity of low-density ω phase in a worked metal must cause *compression* of the residuum of normal lattice structure still within the elastic limit. The evidence of X-rays seems definite, however, in disclosing that the residuum lattice is expanded and not compressed.

Suppose, however, that the atoms in the ω phase are more densely packed than in the normal lattice. As Dean and Gregg have pointed out, the discontinuity is not an actual one corresponding to fissures, so that the atoms of the residuum of normal lattice must be *stretched* apart in a medium of dimensional rigidity in order to compensate for the appearance of the denser ω phase. This hypothesis is in accord with the results of X-ray observations disclosing an expansion of the residual lattice.

The picture of a metallic crystal aggregate with two phases, one the residual lattice with distortions never beyond those comparable to the elastic limit and the other the intercrystalline ω phase with higher atomic packing density, implies that experimentally determined densities show the net result of two internal changes of density; if the two phases are considered to have virtually constant densities within themselves this net change will be determined by the relative quantities of the two phases and their respective average densities. Further, if the average thickness of the ω phase on the intercrystalline boundaries is substantially constant, plainly the change in density of the body as a whole will depend on the crystal size.

As the "stretch" of the residual crystal lattice is limited to some definite value, at which the ω phase is produced, and as the elastic continuity in the elements of the residual lattice is maintained, it may be expected that very finely crystalline metals will increase in density with cold-working, because the increased density of the ω phase will predominate. Conversely, large crystals will normally first show a decrease of density because the amount of material showing lattice distortion is large compared with the quantity of metal in the ω phase, which produces the distortion.

The stress-strain diagram of a single crystal seems to be representable by an exponential relationship, which is approximately parabolic. To ascribe to the residual lattice a definite elastic limit obviously departs from the interpretation of the matrix as consisting of aggregates of single crystals. From the present point of view the criterion of elastic limit is the appearance of new ω phase, and the relationship between quantity of ω phase and quantity of residual lattice material is all-important in determining the external properties of the metal. It must be assumed

that an unstrained polycrystalline metal is not entirely free from the surface phase, but as the crystals grow larger the quantity becomes less. The marked changes in the transition from polycrystalline to single-crystal metal are then associated with the virtual disappearance of the intercrystalline phase.

APPLICATION OF HYPOTHESIS

Two alternative qualitative explanations are now available in an attempt to analyze the shape of the density curves obtained in cold-working copper and iron, as illustrated in the first and second articles of this series. The hypothesis of a denser intercrystalline phase may be compared with an explanation based on mechanical recrystallization. The noteworthy experimental results of Parts I and II that may be discussed in the light of these two hypotheses are:

1. Existence of the minimum of density in drawing copper and iron.
2. Failure to observe the minimum of density in torsional cold-working.
3. Behavior of copper first torsionally cold-worked, then drawn, and finally attaining a substantially constant density.
4. Apparently anomalous behavior of the samples of copper that increased in density.
5. Initial behavior of macrocrystalline copper and the maximum of density.
6. Continual and rapid increase of coercive force in the latter stages of drawing iron.

EXISTENCE OF DENSITY MINIMUM

The attempt may be made to explain the existence of the density minimum in drawing, first on the basis of the idemsorption* hypothesis. Starting with macroscopic crystals, the first production of ω phase shows less material of high density than material of which the lattice has been "distorted," and consequently the density drops. As the crystals grow finer the relative amounts of the two constituents reverse (the amount of lattice distortion is limited and becomes constant with increased cold-work), and the density begins to increase.

Such a simple explanation immediately has to meet the fact that the minimum of density is reached rather far along in the drawing process, whereas the lattice distortion as revealed by X-rays rapidly approaches its constant value when a relatively small amount of cold-work has been done. Thus, for example, Wood found that the "steady state" of distortion had been reached when the reduction was no more than about 20 per

* The word "idemsorption" has been coined to describe concisely the adsorption on crystal faces of a film of the same constituent atoms or molecules as the lattice but having a lower order of crystallographic symmetry than the lattice.

cent in rolling copper, but the minimum of density occurs at some 60 to 70 per cent reduction. If this hypothesis is valid the further assumption must then be made that not all of the matrix material shows the maximum lattice distortion when the point of cold-working has been reached where the measured distortion is constant. The X-rays apparently disclose the amount of distortion (by broadening of the lines), but the amount of material so distorted is determined less readily. Wood's estimate was based on a comparison of peak intensities and presumably involves assumption of distribution ratios. From this point of view the density minimum corresponds to the position where the lattice distortion has become effective upon the maximum (or total) number of matrix crystals or upon the total content of these crystals.

In an attempt to apply the alternative "mechanical-recrystallization" explanation of the density minimum some care must be exercised in defining recrystallization. Crystals obviously do not grow through microscopic or visible size increments during cold-working, though they may at elevated temperatures. In the present instance the formation of crystallites comprises the scope of the term, and supposedly it is brought about "mechanically" by the flow or relative motion of the substance during working.

For such formation it seems clear that a "source" material must be postulated from which the crystallites may be formed. This "source" material may naturally be associated with the ω phase previously postulated. The rate of such crystallite formation at any definite temperature may further be assumed to depend on two factors: the quantity of the ω phase and a probability factor depending upon the relative motion between portions of the source material capable of forming crystallites.

The fact that annealing and recrystallization in the sense of grain growth take place in two stages when cold-worked metals are heated, and the fact that the more severely cold-worked the metal is the lower the primary annealing temperature are entirely consistent with such considerations.

If now the ω phase is denser than the normal lattice, in recrystallizing under the influences of cold-work, it would seem that a further *decrease* of density should occur, but if in so doing the strain is partly removed from the matrix or if the lattice distortion of the matrix is partly corrected the net result may nevertheless be an increase in density if the proportion of ω phase and residual lattice affected are suitable. Further, the ω phase must be located at positions corresponding to discontinuities in the crystal structure, although, as Dean and Gregg have intimated, these locations preferably should be termed "transition zones." These zones, however, are also presumably the locations terminating the blocks of the mosaic. Thus, in spite of the fact that it was concluded in Part I that the gaps in the mosaic were not amenable to filling by a squeezing

action, the possibility of building there a bridge or filling of crystallites under the action of symmetrical deformation must be admitted.

Much of the evidence relative to the fibrous structure of rolled or drawn metals and the "preferred orientation" produced by severe cold-working seems to fit in well with the possibility of such a type of recrystallization. According to Elam these structures cannot be satisfactorily explained on the basis of the distortion of individual crystals, nor can the continued cohesion of the oriented crystals be so explained.

This discussion indicates that the idemsorption hypothesis and the mechanical-recrystallization basis of density minimum may not be independent explanations. The first obviously must permit the possibility of crystallite formation, because if this were prohibited the amount of ω phase could be increased indefinitely with sufficiently severe cold-working, but both X-ray and latent-energy measurements show that these effects are limited. Further, the second explanation is meaningless unless the existence of the source material, i.e., the idemsorption hypothesis, is granted.

LACK OF DENSITY MINIMUM IN TORSIONAL COLD-WORKING

The idemsorption hypothesis, without involving the idea of mechanical recrystallization, does not seem to offer a simple explanation of the failure of torsional cold-working to produce a density minimum. To say that the rupture point of the specimen is reached before the rate of production of ω phase can produce a density increase comparable with the decrease due to lattice distortion does not suffice, although the statement may be correct as far as it goes. If the measurements of residual torsional strain given in Parts I and II may be interpreted to give the magnitude of the lattice distortion, it is plain that this factor has increased rapidly in the early stages of cold-working, and presumably the curves of density should show greater tendency to be concave upwardly than is the case. The measurements of the last stages of torsional cold-work were subject to considerably more error than the earlier stages; although the curves did seem to show some tendency to flatten out, the data are not conclusive enough to justify such an assertion. The conclusion that the density-torsion curves are substantially linear is much more justifiable.

It may be significant that preferred orientation in torsionally cold-worked metals has not been determined satisfactorily. In discussing such work Elam says:

These directions are almost identical with similar directions in drawn wires, and it is open to doubt whether they represent true structures produced by torsion or are due to the fibre structure produced by drawing the original wires. Owing to the nature of the deformation, the experimental difficulties of determining the structure are great.

If the structure does not exist, on the basis of the present theory no recrystallization has occurred.

The fundamental differences in the shape of density curves representing drawn, rolled or twisted wires suggest that the type of symmetry of the relative motion of component parts of the metal affects the appearance of the minimum. This supposition may be tested by comparing the rolling and drawing curves of the first paper. If relations of symmetry are effective, a simple numerical relationship might be expected between the changes of density produced by the two methods. To test this, values of $-\Delta D$ for the drawing operation and values of $-2(\Delta D)$ for the rolling of a similar sample have been plotted against reduction in area, where ΔD is the difference of density at any reduction in area compared to the original

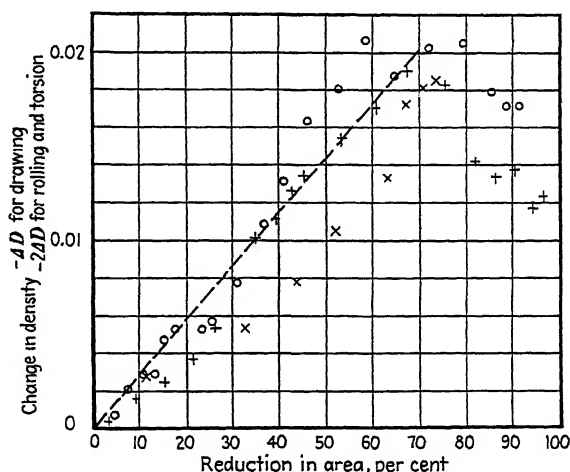


FIG. 8.—VARIATIONS OF DENSITY OF COPPER WITH DIFFERENT METHODS OF COLD-WORKING.

○ Rolling, shows $-2\Delta D$ vs. percentage reduction in area. + Drawing, shows $-\Delta D$ vs. percentage reduction in area. × Torsion, shows $-2\Delta D$ vs. equivalent percentage reduction in area.

density (Fig. 8). Fig. 8 shows that up to the point representing the minimum of density the points for the two samples show substantially the same general relationships, and the maximum change ΔD for drawing is substantially the same as the maximum change of $2(\Delta D)$ for the rolling operation. Beyond the maximum, however, the recovery of density due to rolling seems to be less effective than that due to drawing.

Expression of density changes in torsion in terms comparable to rolling or drawing would be interesting. To do this the values of Nd/L must be expressed in terms of equivalent reduction in area. Consider an element of the specimen of length d (the same as the diameter) taken parallel to the axis of the specimen. The length of this element after torsion corresponding to Nd/L is approximately

$$\sqrt{d^2 + \left(\frac{Nd}{L} \cdot \pi d\right)^2} = d\sqrt{1 + \left(\frac{\pi Nd}{L}\right)^2}.$$

The approximation is introduced in the assumption that the diameter after torsion is the same as before twisting. The ratio $\frac{d}{d\sqrt{1 + \left(\frac{\pi Nd}{L}\right)^2}}$ is

the ratio of the initial to final length; i.e., L_1/L_2 . But in a process of drawing or rolling $\frac{A_2}{A_1} = \frac{L_1}{L_2}$; whence the equivalent percentage of reduction of area in torsion is

$$R_e = 1 - \frac{L_1}{L_2} = 1 - \frac{1}{\sqrt{1 + \left(\frac{\pi Nd}{L}\right)^2}}$$

As this factor is dimensionless, apparently it applies equally to an internal as well as to an external element. In Fig. 8 the values $-2(\Delta D)$ are also plotted against R_e for the torsional cold-working of copper. Unfortunately, in this case the sample was not identical in original density (caused by slightly different annealing) with the drawn and rolled samples. The points show two factors of considerable interest. The curve lies somewhat below the line representing rolling and drawing; its position may be due to the fact that the ω phase is produced more rapidly in torsion, causing a less rapid decrease in density. Of more interest, however, is the fact that the end points, corresponding to the rupture points of the wires under torsion, lie in the same range as the maximum of density change, and the magnitude of the change is again quite near $2(\Delta D)$ for rolling or ΔD for drawing. This fact seems strongly to confirm the assumption that ability to cold-work without rupture beyond the minimum of density in rolling or drawing is due to mechanical recrystallization and that the unsymmetric type of relative motion or flow in torsion, greatly decreasing the probability of mechanical recrystallization, results in rupture before the point is reached at which density increases may be expected.

RESULTS OF DRAWING TORSIONALLY COLD-WORKED COPPER

The explanation relative to the differences between torsional and more symmetric types of deformation is further confirmed by the behavior of torsionally cold-worked wires that later are drawn, as illustrated in the DT curve of Fig. 1. Here it is found that the minimum of density occurs at some 35 per cent reduction in area as compared with 65 to 70 per cent in direct drawing or rolling. The advance in the position of the minimum is attributable to the accumulation in the sample of approximately

50 per cent of the total possible content of ω phase due to the single element of symmetry in the torsion. As the sample was twisted nearly to the limit of strength, it may be assumed that the limit of lattice distortion in one direction had been reached early in the torsion. When drawing was begun the density first decreased further owing to lattice distortion in a second direction.

Several points of interest are related to this test. The wire, after being twisted to a torsion of approximately $Nd/L = 1.25$, was extremely brittle to transverse stresses and could be bent only through a very small angle before rupture. However, it could be drawn readily and *after reaching the minimum* showed high ductility to bending. This can be explained only by recrystallization and the formation of lattice-like bonds between crystal blocks.

The final flattening of the curve beyond the recovery of density is also of great interest. The condition here seems to be a static one, corresponding to a true "steady state." Such a condition implies the equality of two opposite and competing rates. The breaking up of crystals, involving the increased formation of ω phase, is here equal to the rate of mechanical recrystallization, as compared to conditions at the minimum, where, according to the present hypothesis, lattice distortion has been spread through the maximum possible amount of material.

SAMPLES SHOWING AN INCREASE OF DENSITY

The classical theories of work-hardening would have great difficulty in explaining the nature of the changes taking place in the samples that show, both in drawing and torsion, an increase of density from the beginning of cold-working. These samples showed complete softening in the anneal; hence, if lattice distortion is the source of work hardness there could be only a minimum of lattice distortion in these original specimens. It is true that the growth of crystals was not yet visible, and the fibrous structure had been retained throughout the anneal. The difference in structure is the only possible source of the difference in behavior between the sample annealed at 880° and, for example, that annealed at 970° . Explanation of the increase of density by the relief of strain is impossible because at the start there is no strain, and explanation by the filling of intercrystalline voids from a squeezing action is equally unsatisfactory because the original density was greater than samples annealed at a higher temperature, which decreased under similar conditions of deformation. It hardly seems possible that the factors causing the increase in density in the microcrystalline samples are different from those causing the recovery of density beyond the minimum in drawing or rolling.

As the torsional cold-working of macrocrystalline copper failed to show definite evidence for recovery due to mechanical recrystallization,

the increase of density in torsionally cold-working the microcrystalline copper can be attributed principally to an increase in the ω phase; it also confirms the existence of a high-density constituent of the structure produced by deformation. The E and E_m curves of Fig. 4 show that the strain in the microcrystalline copper was less for a given torsion than for the remaining samples, except that it increased more rapidly in the early stages of deformation. The initial behavior is consistent with an early rapid approach to a condition of maximum lattice distortion, both in intensity and amount of material affected. The later behavior seems to show, however, that it cannot be concluded that no mechanical recrystallization whatever occurs in torsion. Rather, the longitudinal fiber structure of the microcrystalline copper, remaining from the original drawing and not removed by the 880° anneal, seems to be transferred in this case to a helical fiber structure. In such a structure mechanical recrystallization must still be possible. With larger crystals, however, with random orientation, it has been shown that the existence of a "preferred orientation" in torsion is difficult to prove.

The magnitude of the increase of density during the drawing of microcrystalline copper is some four times as great as that occurring in torsion. The probability of mechanical recrystallization undoubtedly is greater in drawing, because the "preferred orientation" produced by the original drawing before the anneal and the symmetry of the later deformations would be retained in the absence of grain growth.

MAXIMUM IN DENSITY DURING WORKING

The density maximum illustrated in two curves of Fig. 3 may be tentatively explained in two ways:

1. The initial increase may be due to the filling of empty places in the metals, not as interstitial spaces in the mosaic blocks but as actual cavities caused by grain growth. In Part I the conclusion was reached that after the density of a metal had been lowered by cold-working the mosaic spaces could not be filled directly by a squeezing action. In the present instance the situation is definitely different. Actual grain growth had taken place in the annealing at the higher temperatures. The variation of the initial densities of the samples after annealing shows that the beginning of grain growth first causes a drop in density, which is later recovered, at least in part, upon continued growth of the crystals. As the strains in the material are relieved at much lower temperatures these changes seem possible only through varying degrees of consolidation of the crystals and, by comparison with the densities of vacuum-melted copper or single crystals, show the possibility of spaces in the body.

2. Since the ω phase has been postulated as having a greater density than the lattice, whether or not the samples increase or decrease initially will depend upon whether lattice distortions first grow more or less

rapidly than the increase of density due to ω phase. On this basis the situation depends upon the size and disposition of the crystals.

A clear-cut decision between these alternative explanations of the density maximum does not seem possible without further experimental work. More complete data relative to the density change, attendant upon annealing cold-worked metals, would probably prove significant.

CONTINUED INCREASE OF COERCIVE FORCE IN DRAWING IRON

The rapid increase of coercive force in the later stages of drawing iron wire, in the light of present knowledge, can only be interpreted as indicating that continued and rapid increase of internal crystal surface takes place in this range, corresponding to further decrease of crystal size. The question as to whether this is inconsistent with the hypothesis of mechanical recrystallization must be answered. It has been emphasized that the term "mechanical recrystallization" as here employed does not refer to grain growth but to the bridging of mosaic blocks with a lattice-like structure under the influence of flow in the metal. This recrystallization would have to involve a greater mass of material than the production of new ω phase during the cold-working in order to cause the effectual flattening of the coercive-force curve. It may be supposed that this situation has been attained but once in the present work—in the case of previous twisted wires later drawn, corresponding to the final flattening or "steady-state" condition. Presumably the upward sweep of the coercive-force curve would not be expected to continue indefinitely, for there must be a definite limit both practically and theoretically beyond which further distortion of the lattice cannot be effected mechanically. The curves themselves, however, would show such a condition as a steady state, and the fact that this steady state was not reached except in the case mentioned shows that destruction of the lattice was still taking place at a rate greater than crystallite formation.

That the latter rapid increase of coercive force should occur virtually over the same range as the rapid recovery of density after the minimum in drawing iron cannot be merely a coincidence. It is of particular interest to note that the hypothesis of a denser ω phase, with a lattice distortion that long since has reached its maximum attainable value throughout the mass of the lattice residuum, is the only one apparently that can explain the observed behavior.

EXTERNAL CONFIRMATION OF A DENSER ω PHASE

Recent interest and development in electron diffraction methods offer a new and direct method of studying the nature of metallic crystal surfaces. Although it cannot be doubted that ultimately these methods will be very useful, the exact interpretation of the results so far obtained is none too certain. Thus, one may refer to two published articles

covering approximately the same sort of measurements, one by Darbyshire and Dixit³¹ and the second by Raether³². Both articles disclose substantial evidence of a layer in highly polished metals that gave only two diffuse rings in photographs of electron diffraction. This points "to a complete breaking up of the lattice structure and suggests that the atoms are packed together at their distance of closest approach as in a monatomic liquid," according to Darbyshire and Dixit.

For metals of which measurements were described in both references, it is of interest that practically identical values of d/n , as derived from the Bragg formula, were obtained from the photographs; even more remarkable is the fact that the values of this quantity are practically the same for all metals examined *in the polish layer* and correspond to those expected for the closest packing of metals near the minimum of the atomic volume curve. Thus, for a number of metals farther removed from this minimum the interatomic distances in the polish layer are much less than the normal distances between atoms in the lattice, and consequently the layer is indicated as one of abnormally high density.

The evidence concerning copper does not directly show this high-density ω phase, but the failure may be due to the method used in calculating the interatomic distance. The relationship involved depends on the "form factor" of the intensity curve. Darbyshire and Dixit used the factor 1.18 as the ratio for the first ring between the atomic distance and the value of d calculated from the Bragg formula, but Raether used 1.27 for the same ratio. The first figure is an average estimated by Darbyshire and Dixit, but the uncertainty may be 8 per cent. If the minimum possible value of the factor 1.125 were used the first ring would correspond to an interatomic spacing in the polish layer for copper of 2.52 Å., whereas the normal spacing in the lattice is 2.55 Å.

Clearly, the precision of the interpretation is not yet adequate to definitely prove the existence of the high-density ω phase in copper, but the possibility of the existence of a layer denser than the normal lattice is definitely rendered plausible from these experiments. The results of future refinements of the method, especially the interpretation, will be awaited with great interest.

HEAT CONTENT OF WORKED METALS

That a severely cold-worked metal shows an expansive distortion of the lattice, and that the heat content of a worked metal is greater than the same metal in the annealed state, are observations so adequately supported by a large mass of experimental data as to seem incontrovertible. Parts I and II, however, showed that the expansion of the lattice thermodynamically requires a decrease of heat content. The resultant paradox can be cleared up only by the supposition of the existence in the metal of an accumulation of atoms having a higher heat content than the

normal lattice. These atoms have been termed the " ω phase." Such appellation may be considered unjustifiable because no sharply defined phase boundaries are thought to exist, but convenience and expediency require a concise term for the designation of the total content of atoms not having lattice spacings, either normal or distorted.

A number of more or less indirect comparisons may be made in testing the idemsorption hypothesis and the existence of a ω phase having higher heat content. The simplest of these is to plot the values of density obtained for torsionally cold-worked metals against the corresponding values of "latent energy" as determined by Taylor. Such curves are shown in Fig. 9; apparently the relationships involved are substantially linear in all instances of torsional cold-working presented.

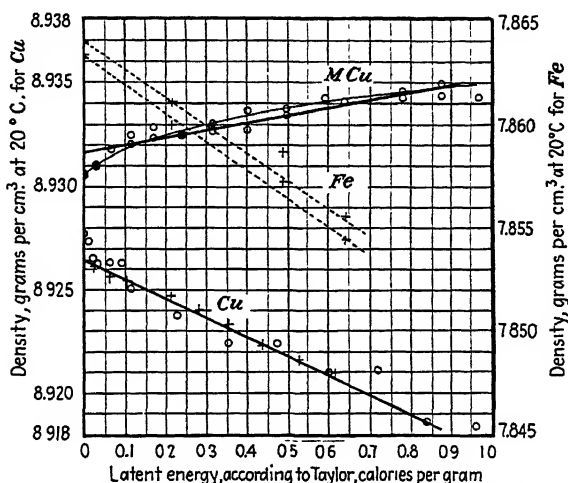


FIG. 9.—OBSERVED DENSITIES IN TORSIONAL COLD-WORK COMPARED WITH "LATENT ENERGIES" AS DETERMINED BY TAYLOR FOR EQUIVALENT AMOUNTS OF TORSION.

Curve *Cu* is for macrocrystalline copper, two samples, and *MCu* is for microcrystalline copper. Dotted lines are for iron.

It cannot be claimed that the demonstration of such relationship is in any sense a direct proof of the hypothesis, but it may be stated that the relationships disclosed are not inconsistent with it. If the density varies approximately linearly with the torsion and the quantity $W - H$ measured by Taylor behaves similarly with respect to torsion, it is clear that the density vs. $(W - H)$ curve must also be approximately linear under any circumstances, and no distinction can be made between cause and effect among the three factors. Nevertheless, if the new phase produced by cold-work may be considered to have characteristic density and heat content just such a linear relationship would be expected.

Further, consider a specific instance of the relationship of thermodynamically calculated and experimentally observed change of heat

content. As shown in Table 5, copper annealed at 1020° C. was apparently nearly saturated with cold-work when the value of $W - H$ (as determined by Taylor) was 0.701 cal. per gram, at which point calculations from the density change showed that the heat content of the lattice should have been reduced by 2.25 cal. per gram. In round figures these are 45 and 143 cal. per gram-atom. On the basis of the indesorption hypothesis, if the lattice heat content has been decreased 143 calories but the net result from experiment has been an increase of 45 calories, the ω phase must have increased in heat content enough to bring about this result. If 1 gram-atom of cold-worked copper is considered, of which x represents the proportion of the ω phase and $1 - x$ the lattice, and if the increase of heat content of the ω phase corresponds to the distortion of the lattice equivalent to fusion, the relationship expected will be

$$143(1 - x) + 45 = 3110x$$

$$x = \frac{188}{3253} = 5.8 \text{ per cent}$$

Wood estimated from X-ray measurements that $\frac{1}{16}$, or 6.25 per cent, of metal in a similar state of cold-work showed the maximum lattice distortion. To assume that this correspondence of order of magnitude is other than fortuitous may seem inconsistent, since Wood's figures presumably refer to the *lattice* and are indicated as expansion, whereas the calculation from heat of fusion involves the ω phase. The assumption implicit in the calculation is that the lattice has given up to the ω phase 143 (1 - x) cal. of its heat content.

The question as to the part of the ω phase that may be represented as adsorbed on the lattice has not been considered, and the high heat-content phase has been referred to as also one of probably higher than normal density. If the amorphous metal had properties similar to those of a liquid, its density, in general, would be expected to be less than for the crystalline material, but the adsorption capacity of a given system of crystal aggregates must be definitely limited. Thus, while only the hypothesis of a higher-density phase explains the various behaviors of the densities of metals when cold-worked, it nevertheless seems necessary also to admit the possibility that only a portion of the ω phase may properly be considered as adsorbed.

In accordance with the calculations above, the lattice has lost 143 cal. per gram-atom, but this energy change is identical with the energy change of the adsorption that caused it, and the total change of $143(1 - x)$ cal. is associated with the heat of adsorption of some unknown quantity of adsorbed material, the content of which probably is less than 5.8 per cent. It is believed that this is also the quantity of heat that must be supplied to "activate" the annealing or crystallite formation.

HEAT OF ACTIVATION

In view of the above, the process of annealing may be tested by the formal application of the Arrhenius equation³³ for the variation of reaction rate constant with temperature. From this equation, $\frac{d \ln K}{dT} = \frac{Q}{RT^2}$ a value of "heat of activation" may be calculated for comparison with known thermal properties.

In attempting such calculation data preferably used are those obtained over long periods at temperatures not too elevated. If the "conversion" is not too high the actual rates for a specific time period may be compared, as the calculation of true "specific rate" usually will involve more data than are given in available measurements of annealing. Further, metals anneal at temperatures much below the point at which considerable grain growth takes place, and this latter process occurring at higher temperatures has only a minor effect on strength or hardness. The interest here is in the "first stage" of the annealing process.

A review of the literature reveals that the work of Carpenter and Smith³⁴ is especially suited for such inquiry. These authors report the percentage loss of work-hardness at various temperatures from 100° to 200° C., after an annealing period of 2.46 years, as follows: 200°, 66; 175°, 51; 150°, 42; 125°, 36; 100°, 23. In applying the Arrhenius expression values of the logarithm of the conversion (percentage loss in hardness) are plotted against the corresponding reciprocal absolute temperatures. Such a chart is shown in Fig. 10, in which the part referring to aluminum shows that only one point of the five fails to fit well into the required linear relationship. This point at 36 per cent loss of hardness would lie upon the line if it were but 32 per cent, a difference not large when considered in relation to the uncertainties of the hardness determination and the possibilities of minor variations in the anneal or original work-hardening of the samples.

The slope of the line of Fig. 10 is 3660 cal. per gram-atom, and this may be compared with the heat of fusion of 2550 ± 100 for aluminum. Thus, the heat requirement to "activate" the conversion of work-hardened aluminum to annealed aluminum is of the same order of magnitude as the heat of fusion but is definitely larger. It should be pointed out, however, that the heat of activation is a hypothetical *absorption* of heat, but if the process of annealing involved only the crystallization of supercooled liquid aluminum it would be accompanied by an evolution of heat and would be of the opposite sign from the heat of activation.

If copper behaved similarly, one might expect a heat of activation of near 4500 cal., since the heat of fusion is 3110. Actual data on copper are not well suited to the calculation and lead to some surprising discrepancies. Thus, Pilling and Halliwell's data³⁵ on the tensile strength

of variously annealed samples do indeed show the required linear relationship, as indicated in Fig. 10, which shows two sets of samples, one obtained from copper reduced 53.2 per cent in thickness and the second, 71.2 per cent. Although the more severely cold-worked copper shows an actual annealing rate some three or four times greater than the less severely worked samples the slope of the two lines is the same and corresponds to 35,000 cal. per gram-atom. Such an amount of heat is inconceivable as being necessary to "activate" the softening of a single gram-

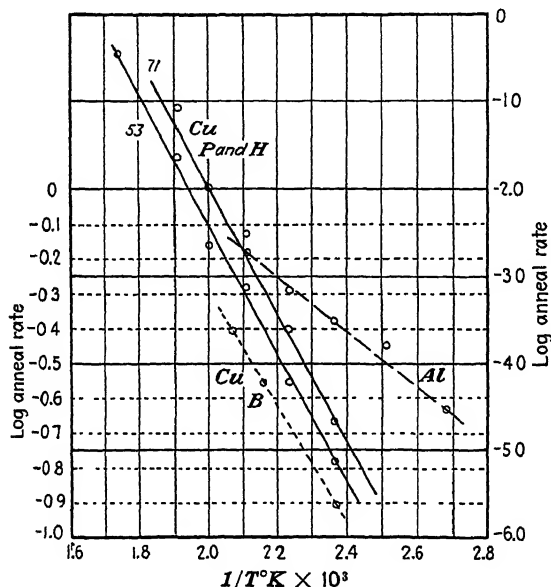


FIG. 10.—DATA FOR CALCULATING "HEAT OF ACTIVATION" OF ANNEALING OF ALUMINUM AND COPPER, FROM SLOPE OF $\log K$ vs. $1/T$ PLOT.

Al, aluminum, percentage loss of hardness per unit time. Cu, P and H, data of Pilling and Halliwell for loss of tensile strength per unit time of rolled copper, 53 and 71 per cent reductions in thickness. Cu B, part of data of Bradley for loss of tensile strength per unit time of drawn copper wires.

atom of copper; it would suffice to raise the temperature of this amount of copper to the melting point, fuse it, vaporize it and finally bring the gas to near 4000° C. One may speculate, however, upon the apparent similarity of this quantity of heat to the heat of formation of cuprous oxide, which is probably between 37,000 and 38,000 cal. These authors give the oxygen content of their samples as 0.066 per cent and the grain size in the partly annealed condition, 0.01 to 0.02 mm. The number of surface atoms compared to the total number of atoms in particles of 0.02 mm. is approximately 0.04 per cent, and the actual oxygen content of 0.066 per cent is equivalent to approximately 0.26 per cent of all the atoms being oxygen; whence it is clear that enough oxygen is present to

completely cover with an adsorbed layer of oxygen or cuprous oxide crystals somewhat smaller than those indicated.

Other data on the annealing of copper are available as, for example, those presented for the annealing of hard-drawn wire by J. C. Bradley³⁶ in a discussion of a paper by Zickrick and Dean. The lower-temperature parts of the anneal tests presented show anomalous behavior, but the data for the highest-temperature tests are insufficient to calculate specific reaction rates; several points in the middle range, however, may be plotted to show an apparent heat of activation of 7850 cal. per gram-atom. The oxygen content of the wire is not given. The data of Pilling and Halliwell show that the amount of cold-work does not affect the heat of activation as calculated from the variation of annealing rate with temperature. This argument may be extended to show that grain size is also not a factor, although obviously it does affect the magnitude of the actual annealing rate. It is difficult to explain the discrepancy between various values of heat of activation on any basis other than the possible effect of impurities that may adsorb on the internal crystal surfaces. Thus, the minimum value of heat of activation may be assumed to be some quantity slightly greater than the heat of fusion and may pertain to the purest samples, but in the presence of impurities, which may adsorb at the crystal surfaces, greatly increased quantities of heat may be necessary to "activate" the dissociation.

If, thus, the true heat of activation of copper lies between 4500 and 7850 cal., and if in the previous numerical example the disappearance of the adsorbed layer (by crystallite formation) requires that 143 cal. be returned by the ω phase to the lattice, then the estimated amount of adsorbed film is $143/7850 = 1.8$ per cent to $143/4500 = 3.2$ per cent. As a preliminary estimate, it seems that $1/4$ to $1/2$ of the ω phase may have been adsorbed in this particular example.

The values of $W - H$ vs. ΔH of Tables 5 and 6, showing torsionally-worked copper, are plotted in Fig. 11. The lines show that the initial relationship is approximately linear, but the curves flatten off at the lower end—at this point $W - H$ is increasing without further equivalent increase of ΔH . Such behavior can now be interpreted. ΔH refers to the lattice, which has now become saturated, but the net increase in heat content, $W - H$, continues to increase because new ω phase is still being produced. Copper annealed at the higher temperatures and having larger crystals shows the more rapid decrease of ΔH and a greater final decrease of ΔH , which is entirely consistent with the previous delineation of the idemisorption hypothesis.

ENTROPY OF COLD-WORKED METALS

According to formula 10, the increase of entropy of the lattice is given by $\Delta S = \frac{\alpha}{\beta} \Delta V$. The maximum value of ΔV for torsional cold-

working of this particular sample was approximately $7 \cdot 10^{-5}$ (Table 5), whence ΔS is calculated to be $4.75 \cdot 10^{-3}$ c.c. at. per degree per gram, corresponding to 0.007 cal. per degree per gram-atom. If the ω phase could be regarded as liquid metal the entropy increase at the melting point would be 2.3 units, and if, as calculated above, 1 gram-atom of worked copper contained 5.8 per cent ω phase the apparent increase of entropy due to this factor should be approximately 0.13 units. The first of these figures, referring to the lattice, is beyond the limit of present experimental disclosure, but the second might cause an increase of specific heat of the order of magnitude of a per cent, which should be easily detectable. Anderson, however, showed¹ that measurable differences

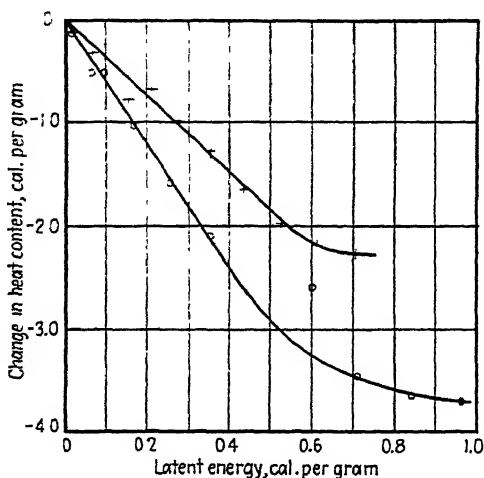


FIG. 11.—RELATIONSHIP BETWEEN CHANGE OF HEAT CONTENT OF TWO SAMPLES OF TORSIONALLY COLD-WORKED COPPER CALCULATED FROM OBSERVED CHANGE OF SPECIFIC VOLUME, COMPARED TO TAYLOR'S MEASUREMENTS OF "LATENT ENERGY" FOR EQUIVALENT AMOUNTS OF TORSION.

did not exist from liquid-air temperatures to near room temperatures. Either the expected difference at the melting point has been compensated by the specific heats in the interval 300° to 1083° C., or an internal compensation has taken place. The measured difference, which may be taken as zero, is the *net* result. The formation of adsorbed film, resulting in less "randomness" than in the liquid, points to the conclusion that the entropy of the adsorbed portion was certainly less than that of the liquid and probably less than that of the lattice. If the latter were true the failure to observe a change of specific heat is explainable, but a quantitative interpretation clearly requires much more conclusive data than are now available as to the distribution of material of different energy content in worked metals. This discussion may be taken to show that the actual situation is more complicated than expected and that there is no probable simple explanation of observed behavior.

FREE ENERGY OF WORKED METALS

Elam briefly discusses measurements of solution tension of worked metals as compared to annealed. The application of formula 11, $\Delta F = -\frac{\Delta V}{\beta}$, shows that in the same example of torsionally cold-worked wire as previously used the free-energy change due to maximum lattice distortion would be a decrease of the order of 0.0145 cal. per gram-atom. The maximum electromotive force ascribable to the lattice when worked copper is compared to annealed copper in a reversible cell would not be more than of the order of a microvolt. Actually, such cells show voltages of 2 to 10 millivolts.

The electromotive force of a series of wires drawn in 12 steps to approximately 90 per cent reduction in area and compared to the same copper in annealed state, using neutral 0.05 normal CuSO_4 for electrolyte, did not show definite variation of electromotive force with degree of cold-work or density. Soon after the cells were set up the average value was 5.24 ± 0.77 mv., of which only the first three steps—3, 9 and 15 per cent reduction—showed less than the average (3.51, 3.82 and 4.28 mv., respectively). After nine months in a thermostat at 25°C . the same cells showed an average of 1.82 ± 0.37 mv., but none of the initial samples showed an electromotive force differing from the average by more than ± 0.37 .

It is very doubtful whether these are reversible cells. They are highly photosensitive, and the reference electrode of annealed copper is by no means reproducible, since several specimens of the same wire showed variations of several tenths millivolts when compared with each other. Further, the electromotive force developed is affected by the hydrogen-ion concentration. It is of interest, however, that a cell of this type, when connected directly to a millivoltmeter of 1000 ohms resistance, continued to furnish current at a rate of 1.5 to 2 microamperes for nine months continuously, although initially the apparent voltage was 5 to 6 mv. At an average current output of 2 microamperes this cell should have dissolved 15 mg. of copper from the worked electrode, which was a rolled strip of which the submerged portion weighed approximately 0.33 gram, whence approximately 4.5 per cent of the electrode was dissolved. If only the ω phase should dissolve, an ultimate check on the content of the high-energy phase should be possible.

The cells behave, however, as if the worked electrode were a composite of two constituents of slightly different solution tension. If so, it may not be possible to dissolve only the ω phase in this manner. All that can be said at present is that the effective electromotive force is much greater than would seem possible from lattice distortion only; whence one must conclude that there is present in the worked electrode a form of copper

of higher energy content than corresponds to the lattice in its state of maximum distortion.

WORK-HARDENING AND DENSITY CHANGES

The complexity of the density changes occurring in the cold-working of metals clearly precludes any simple functional relationship between the degree of work-hardening and density over the entire range of possible deformation. The undeniable fact of lattice distortion, as revealed by X-rays, and its general correlation to the initial density changes further disallow the casual description of observed density changes as merely the result of production and filling of intermosaic voids. Before any general comparison can be made between observed changes of density and the progress of work-hardening some quantitative theory of work-hardening is required. This has only recently become possible through the brilliant and ingenious analysis of Taylor³⁷.

According to Taylor's theory the stress-strain relationships of a single crystal are parabolic, expressible by the equation

$$\frac{S - S_T}{\mu\sqrt{s}} = K\sqrt{\frac{\lambda}{L}}$$

where S is the stress during working, S_T is a finite stress, which must be attained before a single "dislocation" can migrate in a perfect crystal, μ is the coefficient of rigidity from elastic theory, s is the strain, λ is the interatomic spacing, and L is a length associated with the distance a "dislocation" may move, which has been correlated with an approximate dimension of 10^{-4} cm. corresponding to the supposed mosaic-block sizes.

To visualize the process of cold-working, Taylor postulates that the stress S varies as $\mu\lambda\sqrt{N}$, where N is the number of pairs of dislocation lines per unit volume and where the proportionality constants may have the maximum value of $1/\pi$. As the lines represented by N presumably extend only in the direction of dislocation N is also the number per unit area, as is dimensionally required by the formula. Further, the strain is $s = N\lambda L$. If it is assumed that each "dislocation" is associated with a definite average volume change, the strain s will be proportionate to the density.

In torsional cold-work the plot of density vs. Nd/L is in all instances, except for microcrystalline copper, increasing in density, substantially linear. The torsion expressed as Nd/L differs from the average strain only by the factor $\pi/2$, and it is clear that the linear relationship is consistent with Taylor's development.

Consider the strain in wire drawing. Experiment shows that in the initial stages of drawing the assumption that the axis of the wire is fixed and that concentric outer shells move parallel with respect to the axis is a

close approximation to the relative motion of parts of the material. To analyze the density changes as dependent on strain, the relationship between the strain and the area of cross section of wire being drawn is desirable. For purposes of calculation the volume of the wire may be regarded as constant. By definition $ds = \frac{2dl}{D}$, where dl is the relative axial motion of any concentric shell of diameter D . Further, the volume $V = \frac{\pi D^2 l}{4} = Al$, where A is the cross-sectional area of the wire.

Then $A dl + l dA = 0$, if $V = \text{constant}$

$$dl = -\frac{V}{A^2} dA$$

Further

$$\begin{aligned} \int_0^s ds &= - \int_{A_1}^{A_2} \frac{2V}{D A^2} dA \\ &= - \int_{A_1}^{A_2} \frac{\pi^{\frac{1}{2}} V}{A^{\frac{3}{2}}} dA \\ s &= \frac{2}{3} V \sqrt{\pi} \left(\frac{1}{A_2^{\frac{3}{2}}} - \frac{1}{A_1^{\frac{3}{2}}} \right) \end{aligned}$$

In view of the latter equation it appears that the abscissas of the density-change curves for wire drawing might preferably be the quantity $\left(\frac{1}{A_2^{\frac{3}{2}}} - \frac{1}{A_1^{\frac{3}{2}}} \right)$ rather than the simple reduction in area. Fig. 12 shows the data for the drawing of copper given in Table 1, plotted in this manner. This chart shows that the points do initially approximate closely the linear relationship required by the theory, the deviations being of about the same order as those illustrating the parabolic stress-strain relationship used by Taylor in developing his analysis.

The parabolic curves used by Taylor show that the upper parts of the stress-strain curve consistently give less actual stress than would be expected from the functional relationship; since S varies as $\mu \lambda \sqrt{N}$, where it may be supposed that μ and λ are fixed for a given material, it must be concluded that N no longer increases at the expected rates when the metal is very severely worked. Similarly, the lower end of the curve in Fig. 12 shows that the density is no longer increasing at a rate proportionate to strain, which may be attributed to the fact that N cannot increase indefinitely, since there cannot be more "dislocations" than there are atoms.

The point at which the linear relationship fails in drawing corresponds to $\left(\frac{1}{A_2^{\frac{3}{2}}} - \frac{1}{A_1^{\frac{3}{2}}} \right) = 3$ (cm. units); so considering a cubic centimeter, the strain is $\frac{2}{3} \sqrt{\pi} = 1.18$ times as great, or $s = 3.5$ approximately. In the

torsional cold-working experiments on the same wire failure occurred in the range $Nd/L = 1.0 - 1.2$. The mean strain is $\frac{\pi Nd}{2L}$, the maximum $\frac{\pi Nd}{L}$, or $s = 1.1\pi = 3.5$. The maximum possible strain in torsion is then identical in magnitude with the strain at the point of departure from a linear density-strain relationship in drawing.

What can now be said about the increase of density beyond the minimum in drawing or rolling or the behavior of the "microcrystalline"

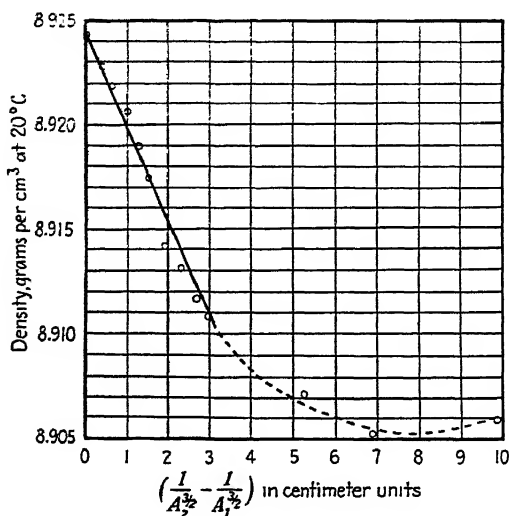


FIG. 12.—"RECTIFICATION" OF INITIAL PORTION OF CURVE SHOWING CHANGE OF DENSITY OF MACROCRYSTALLINE COPPER IN DRAWING.

Abscissas are differences of reciprocal three-halves power of initial and final areas of wire expressed in centimeter units, and are proportional to theoretical strain.

samples? Referring to the general form of Taylor's equation

$$\frac{S}{\mu\sqrt{s}} = K\sqrt{\frac{\lambda}{L}},$$

s is obviously an independent variable, depending only on

the extent and geometry of the deformation, and presumably may increase (in drawing) almost indefinitely, or until rupture occurs. If S is a measure of hardness and becomes substantially constant before failure occurs, L must increase in the later stages of deformation. Further,

if $N = \frac{1}{\lambda} \frac{s}{L}$, where λ is constant, N may in this range either become

approximately constant or decrease, depending upon whether the increase in s is equal to or less rapid than the increase in L . The increase of L so postulated corresponds to the mechanical recrystallization (formation of crystallites) previously discussed and further corresponds to an increase of

density beyond the minimum if each dislocation is associated with a specific average volume change. The possibility of a decrease in N corresponds to "work-softening."

The "microcrystalline" copper, increasing in density at the beginning of the cold-work, became hardened; therefore, if Taylor's hypothesis can be applied here the form $S = K\lambda\sqrt{N}$ shows that N was increasing throughout these tests, although at a less rapid rate as the deformation increased. In this instance the increase in density cannot be explained on the basis of the volume change associated with dislocations; in fact, it may be concluded that, if Taylor's hypothesis is valid and the dislocations are associated with a decrease of density, in this sample some constituent must be formed in large enough amounts to more than overbalance the decrease resulting from the increasing number of dislocations. This points to the necessity of some further explanation, such as was suggested in the idemisorption hypothesis.

Taylor interprets length L as associated with the dimensions of mosaic blocks, but the variation of stress-strain relationship with temperature is interpreted as the variation of opacity of the boundaries to dislocations with temperature. This explanation seems to imply a type of potential barrier at the boundaries greater than that existing in the normal lattice; such a condition may be assumed to be the result of idemisorption or its equivalent.

PSEUDO-MOLECULE THEORY OF DEAN AND GREGG

The conclusion that an adsorbed film may exist at intercrystalline boundaries, in which the interatomic forces are necessarily greater than in the interior of the lattice, has many points of similarity with the "pseudo-molecule" theory of Dean and Gregg, although as an explanation of work-hardening the theory and mathematical analysis of Taylor seems likely to be of considerably greater value, as it permits for the first time a quantitative approach to the fundamental problem and is capable of reaching a wider variety of phenomena. Work-hardening reaches its full state early in the history of a deformation process, and in this field Taylor's theory, in spite of its admittedly incomplete form, has made valuable and significant progress. The magnitude of the strains through which Taylor's parabolic expression holds is small, however, compared with the extent of deformation to which a metal may be subjected without rupture by drawing, rolling, and even torsional processes. As has been shown, complex changes of density, etc., are still occurring in the range beyond the validity of the parabolic expression, so that it is certain that further changes may take place unaccounted for by Taylor's analysis. It is in this range, especially in connection with electrical and magnetic changes, that the prophetic words of Dean and Gregg referred to earlier seem likely to be borne out.

SUMMARY AND CONCLUSION OF PART III

On the basis of present experiments, compacted metallic crystal aggregates, as typical of annealed rolled metals, show changes in density that are functional rather than random with further increasing cold-work. The original density in the annealed state may be somewhat random as affected by mosaic-block structure.

Observed density changes are consistent, to a certain extent, with available data on lattice distortion.

It appears logically necessary to describe lattice distortion as the result rather than the cause of changes taking place in the deformation of metallic crystals. If lattice distortion is the result of the changes taking place in cold-working, X-ray and density measurements can be explained only by the existence in metallic crystal aggregates of a certain portion of material of density higher than normal, presumably located in the zones of intercrystalline boundaries and having the nature in part of an adsorbed film. This has been termed the "idemsorption hypothesis."

The use of measured changes of specific volume to calculate thermodynamically the expected changes of heat content, entropy and free energy attendant upon lattice distortion shows that thermal changes resulting from such distortion do not adequately explain observed discrepancies between work and heat in the deformation of metals.

A semiquantitative explanation of observed behavior requires postulation of the existence in the metal of the equivalent of a new phase having a higher heat-and-free-energy content than the lattice. Such a hypothesis differs from the Beilby "amorphous-cement" theory in that the new phase is thought to be a denser adsorbed film rather than a supercooled liquid of lower density than the lattice and has little to do with work-hardening phenomena except to create at intercrystalline boundaries a potential barrier only partly permeable at ordinary temperatures to atomic dislocation.

The idemsorption hypothesis is not inconsistent with Taylor's dislocation theory of strain-hardening; in fact, it is complementary to it.

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DISCUSSION

(F. N. Rhines presiding)

C. H. DESCH,* Teddington, Middlesex, England (written discussion).—Mr. Maier's paper is particularly valuable for its accurate determinations of density. It is, however, unfortunate that the materials used were not of more exactly known purity, as these changes of density are greatly affected by the presence of small quantities of foreign elements. The copper is said to have been commercial copper wire, and the iron was Armco iron. The latter is not a homogeneous material, but has a segregated center, so that the properties throughout a section are not uniform. This circumstance may account for the difficulty of interpreting some of the results where the differences in density are very small. The great difficulty of obtaining satisfactory results for the quantity of energy stored during the cold-working of a metal has been brought out by the author. In addition to the experimental work quoted, attempts have been made in the writer's laboratory at Sheffield to determine this quantity by measuring the heat of solution of iron and copper in the cold-worked and in the annealed condition^{38, 39}. This method, although of high precision, suffers from the defect that the heat of solution in any available solvent is great compared with the quantity to be measured, so that the energy is obtained only from the small difference between two large quantities. The results, however, are in qualitative agreement with those obtained by Taylor by an entirely different method. It is much more difficult, however, to make quantitative deductions.

The writer is still of opinion that the Beilby hypothesis is by no means obsolete. It is necessary to distinguish between the theory of Beilby that the crystalline structure is broken down and a vitreous phase is produced by cold-working, and the later theory of Rosenham that the crystals even in a cast metal are originally separated by an amorphous layer. The two are really independent, and the writer has never accepted the view of the amorphous intercrystalline layer, but has always considered that the vitreous phase is only produced by severe deformation. This phase must be of lower density. It cannot, of course, be detected by X-rays, but recent work on the surface of polished metals examined by means of diffracted beams of electrons certainly shows that the existence of a vitreous layer on the polished surface is highly probable⁴⁰.

The theory of the cold-working of metals is far from complete, but Mr. Maier has made a valuable contribution to the subject, and his results must be taken into consideration in any future discussion.

R. S. DEAN,† Washington, D. C. (written discussion).—Mr. Maier has definitely shown that while the mean lattice-parameter changes on cold-work are consistent with

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³⁸ C. J. Smith: *Proc. Roy. Soc.* (1929) **125A**, 619.

³⁹ R. W. France: *Trans. Faraday Soc.* (1934) **30**, 450.

⁴⁰ Symposium on Thin Films. *Trans. Faraday Soc.* (1935) **31**.

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density lowering, the energy changes are not at all consistent with the assumption that these lattice-parameter changes are due to elastic distortion. It is therefore necessary to assume that some of the atoms in cold-worked metal are in a high energy state.

Mr. Maier rejects the simple conclusion that the high-energy atoms are those (6 per cent) which W. A. Wood has found to be markedly further apart and concludes that the high-energy atoms are actually closer together. His reason for this, that if a less dense phase were formed the "dimensional rigidity" of the remaining lattice would require that it be compressed, does not seem well taken. Dimensional rigidity in a material during the process of deformation is hard to visualize. Mr. Maier's other basis for assuming a more dense phase—the increase in density on extreme cold-work—may be as well explained by flow in the new phase itself, a process that Mr. Maier has recognized under the name "mechanical recrystallization."

A study of Mr. Maier's experimental data leads to the following conclusions:

1. Cold-working may be defined as the production of internal surface by shear.
2. This internal surface is a linear function of the amount of deformation $\left[\frac{ND}{L} \text{ or } \left(\frac{1}{A_2^{3/2}} - \frac{1}{A_1^{3/2}} \right) \right]$ up to the limit of torsional deformation.
3. The lattice is expanded to the elastic limit by shear and is maintained in this expanded condition by the cementing action of a new phase, which occurs at the internal surface and is proportional in amount to this surface.
4. This new phase is less dense but has much higher energy than the lattice, hence the density decrease and energy increase are linear functions of internal surface (measured by coercive force or $\frac{ND}{L}$).
5. Above the limit of torsional deformation the increase of internal surface (as indicated by H_c) with cold-work (as indicated by reduction in area) is more rapid but the new phase is itself deformed with increase in density.
6. The formation of pseudomolecules by the sharing of electrons between metal ions at the internal surface as postulated by Dean and Gregg will explain all the above facts, including the ability to be broken down by a high degree of deformation with the formation of a more closely packed arrangement of ions.

V. H. STORR,* Teddington, Middlesex, England (written discussion).—The thermodynamic methods of Gibbs, although elegant, have often resulted in errors when used by later writers who have ignored essential conditions restricting the validity of many equations. The commonest of such conditions is that the changes to which some equation refers must be reversible. This condition would appear to have been overlooked by Mr. Maier. It is, therefore, desirable to show at what stage in the reasoning the condition becomes necessary.

Equation 4 (p. 122) is correct, but applies only to *reversible* changes in the metal. This may be seen from the following derivation of the equation from first principles. For *any* change in a system we may write

$$dE = dQ - dA \quad [1]$$

where dE is the increase in the energy of the system, dQ is the heat absorbed by the system, and dA represents the loss of energy of the system which is not in the form of heat.

For *reversible* changes we may write

$$dQ = TdS \quad [2]$$

where S is the entropy of the system, and for changes in systems whose state is determined by a knowledge of the volume V and the temperature T , we may also write

* National Physical Laboratory.

$$dA = PdV \quad [3]$$

where P is the pressure.

From equations 1, 2 and 3, we find

$$dE = TdS - PdV \quad [4]$$

$$\text{or} \quad dS = \frac{1}{T}dE + \frac{P}{T}dV \quad [5]$$

$$\text{but} \quad dE = \frac{\partial E}{\partial T}dT + \frac{\partial E}{\partial V}dV \quad [6]$$

$$\text{Whence from eq. 5,} \quad dS = \frac{1}{T} \cdot \frac{\partial E}{\partial T}dT + \left(\frac{1}{T} \cdot \frac{\partial E}{\partial V} + \frac{P}{T} \right) dV \quad [7]$$

$$\text{From eq. 7,} \quad \left. \begin{aligned} \frac{\partial S}{\partial T} &= \frac{1}{T} \cdot \frac{\partial E}{\partial T} \\ \frac{\partial S}{\partial V} &= \frac{1}{T} \cdot \frac{\partial E}{\partial V} + \frac{P}{T} \end{aligned} \right\} \quad [8]$$

$$\text{and since} \quad \frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

we find from eq. 8,

$$\frac{1}{T} \cdot \frac{\partial^2 E}{\partial V \partial T} = -\frac{1}{T^2} \cdot \frac{\partial E}{\partial V} + \frac{1}{T} \cdot \frac{\partial^2 E}{\partial T \partial V} + \frac{T \frac{\partial P}{\partial T} - P}{T^2} \quad [9]$$

But $\frac{\partial^2 E}{\partial V \partial T} = \frac{\partial^2 E}{\partial T \partial V}$, whence from eq. 9,

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad [10]$$

$$\text{Now} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\text{and} \quad \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\text{whence} \quad \alpha/\beta = \left(\frac{\partial V}{\partial T} \right)_P / \left(\frac{\partial V}{\partial P} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad [11]$$

From eqs. 10 and 11,

$$\left(\frac{\partial E}{\partial V} \right)_T = T \frac{\alpha}{\beta} - P \quad [12]$$

which is equation 4 of the original paper.

It may be written

$$\partial E = \left(T \frac{\alpha}{\beta} - P \right) \partial V \quad [13]$$

where ∂E and ∂V refer to changes at constant temperature.

Equation 13 is the correct form of equation 7 of the original paper. The mistake in the latter equation results from the statement that

$$-P = \frac{V - V_0}{V_0 \beta}$$

instead of

$$P_0 - P = \frac{V - V_0}{V_0 \beta}$$

From the derivation of equation 13, we see that it is inapplicable to *irreversible* processes for which equation 2 is invalid. It is also inapplicable to systems whose changes of state require the values of more than two variables for their determination.

It is, therefore, for two reasons inapplicable to the *permanent* change of volume of any substance, where by "permanent change of volume" is meant a change of volume that remains after the original conditions of temperature and pressure have been restored. The changes of volume resulting from the cold-working of metals are of this kind.

Similar remarks apply to the other thermodynamical equations in the original paper, reversibility of the processes considered being assumed in connection with any equation involving the conception of entropy.

H. E. FLANDERS,* Middletown, Ohio (written discussion).—I am much interested in the conclusion of the author that "A semiquantitative explanation of observed behavior requires postulation of the existence in the metal of the equivalent of a new phase having a higher heat-and-free-energy content than the lattice."

In the development of the phase rule, Willard Gibbs considered the conditions existing at the boundaries of phases, but since these would have no effect on the thermodynamic considerations about the phases usually considered, the factors including these boundary areas were eliminated. Rideal⁴¹ makes the following statement in his opening paragraph: "Under certain circumstances at least, and perhaps always, the boundary is not simply a geometrical surface upon one side of which there is one phase of uniform properties and on the other a second phase, everywhere distinct from the first and homogeneous in itself; nor, again, do the contiguous phases shade, as might equally well be supposed, rapidly but continuously one into the other, so that the boundary would have to be considered as a more or less arbitrary mathematical definition rather than a physical entity: it lies in a film or lamina of finite though minute thickness consisting of an entirely new phase of definite and measurable properties." The bulk of the book is a treatment of the considerations of this boundary layer as it exists in equilibrium with the other phases.

There seems to be no reason for not going one step further and assuming that the discontinuities in ordinary crystalline materials are positions of a boundary phase. Some very interesting deductions can be made from such a premise. For the sake of brevity, let us assume a homogeneous alloy as usually considered existing as an aggregate of crystal grains. The boundaries of these grains are considered as separate phases with properties quite different from those in the crystal proper. There are differences in chemical composition due to the differences in solubility existing and, as equilibrium is approached, distribution coefficients for each of the constituents become more nearly satisfied.

If the alloy is cold-worked, rupture of the grains takes place, presumably along cleavage planes. This results in more boundary phase which, at the time of formation, has the composition of the crystal from which it forms and is not in equilibrium with it. Diffusion processes tend to satisfy this lack of equilibrium, resulting in a change in the property of the boundary phase as its composition changes toward its equilibrium state. If the alloy is supersaturated with respect to any constituent, precipitation is most easy in the boundary phase, a commonly recognized fact, and if cold-work has been accomplished, a general precipitation in the newly formed phase locations may occur. This may be the mechanism of rapid aging in cold-worked metals. If precipitation is forced within the grain, due to sufficient supersaturation, a new boundary phase is formed between the precipitate and the crystal, resulting now

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⁴¹ Rideal: Surface Chemistry, Ed. 2.

in three phases. The condition of precipitation requires that the free energy decrease due to precipitation be greater than the free energy increase due to boundary-phase formation. This results in a definite minimum size of precipitate for any given set of conditions. If the boundary phase already exists, precipitation is quite direct, as only compositional changes in the phase are necessary to maintain equilibrium and, when opportunity is given, diffusion to these boundaries generally takes place.

The close relationship that exists between the extent of boundary phase and physical properties indicates, as discussed in the paper, that the nature of these properties is largely controlled by this boundary phase; and inasmuch as this boundary phase is a position of relatively high free energy content, a decrease of free energy occurs when it disappears. A gradual change of properties takes place as this process—grain growth or coagulation of precipitate—occurs and the control of these changes is the work of practical metallurgists.

C. G. MAIER (written discussion).—Dr. Desch's comments are valuable and pertinent. The author is fully aware of the desirability of extending measurements of precise densities in the process of deformation to a wider variety of samples, and especially very pure metals, and those of a known state of crystal aggregation, including *single crystals*. Circumstances prevent his undertaking such measurements himself, but it is suggested that such work might be admirably suited as a subject for advanced student research.

The annealing (and recrystallization) in the samples used by the author was purposely severe, resulting in the noted purification (by sublimation) and probable complete uniformity of structure in a given set. The fact that densities greater than those calculated from "precision" lattice parameters were found for copper, and identical with those for iron, would seem to indicate that at least in these instances impurities were not producing marked variations of density.

Metallurgists in this country have rarely distinguished between the variants of the Beilby theory, and the author is indebted to Dr. Desch for correcting him, and making these alternatives clear.

Mr. Stott's criticism does not seem valid to the author. It is obviously possible to calculate any intrinsic property of a material by thermodynamic processes based on reversibility, even when the actual process by which this state is reached may not be reversible. In fact, it may be true that no natural processes are, strictly considered, reversible, although some approach closely to this condition. One may reach a certain quality of vapor in a heat engine which differs materially in its action from the "reversible" cycle that is the thermodynamic abstraction, but the intrinsic qualities of that vapor are accurately determined by the calculation based on reversibility, no matter what processes were used to reach this state. This presupposes that the state is uniquely determined by three independent variables.

It was unnecessary for Mr. Stott to confirm equation 4 of the author's paper, since it is merely the Bridgman equation with α and β replacing the partial differential coefficients. Equation 7 is obviously an approximation to equation 4 obtained by introducing $-P = \frac{V - V_0}{V_0\beta}$ for the P in the original equation and integrating. Stott's version $P_0 - P = \frac{V - V_0}{V_0\beta}$ would be necessary if the equations were referring to a gaseous material, but the approximations introduced by taking $P_0 = 0$ and by neglecting ΔV^2 with respect to $2V_0\Delta V$ would certainly seem justifiable in connection with metals and solids.

Concerning the justification of the general method of approaching the problem, the author first shows that measured density changes in cold-working are consistent, as far as the data can be interpreted within the results of lattice-parameter measure-

ments. Such volume changes necessarily involve a change of the internal energy of the system, and it is perfectly proper to calculate by ordinary thermodynamic methods the difference in the two known states due to such volume change, for comparison with measured values. These calculations show that the amount of elastically stored energy cannot account for directly measured increases of internal energy, whence some other means of energy storage must be postulated. The author believes his method of calculation more valid than that of Wood (see p. 137).

Mr. Dean has chosen to ignore the samples of well annealed copper which showed only an increase of density, both in drawing and torsion. Since the initial density was higher than for samples decreasing in density, the presence of gaps in the structure, fillable by deformation, seems improbable. The author does not agree that Mr. Dean's six conclusions are indicated by the experimental work.

Creep and Twinning in Zinc Single Crystals

BY RICHARD F. MILLER,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February, 1936)

RECENT studies of creep have made it apparent that plastic deformation may occur in metals under stresses less than the elastic limit as determined from short-time tests. In summarizing conclusions drawn from creep tests by various investigators, Tapsell^{1†} said: "It is evident that if a material has a true elastic range, the elastic limit must represent the maximum stress for no creep."

The presence of a definite elastic limit, represented in single crystals by a critical or threshold shearing stress, is claimed by Schmid², Elam³ and others who have investigated the plastic deformation of single crystals. However, this "law of critical shearing stress" was determined² from short-time tests, and the measurement of the deformation was made with apparatus primarily designed to observe large amounts of plastic deformation, not to detect elastic changes.

Experimental data recently obtained with highly sensitive instruments by A. W. Hanson⁴ on zinc and by Podaschewsky⁵ on rock salt indicate that the elastic range in single crystals is considerably narrower than formerly was supposed. Moreover, a theoretical possibility of permanent deformation, under the influence of even the smallest shear stress in single crystals above a certain temperature (T_d), has been developed by G. I. Taylor⁶.

This evidence seemed to warrant an examination of the elastic limit in large single crystals by means of creep tests. The first metal chosen for examination was zinc.

APPARATUS

The creep-testing apparatus developed for this work is shown in Figs. 1 and 2. The extensometer *A* is sensitive enough to detect changes in length of $\pm 3.3 \times 10^{-6}$ in. per in., and yet can be used into the plastic range without injury to the apparatus. The specimen,

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† References are at the end of the paper.

held in steel grips, is suspended from a ball and socket joint in a heavy steel framework *B*. The specimen is surrounded by an electric furnace *C*, where the temperature can be controlled within $\pm 1^\circ \text{C}$. by a Brown recording potentiometer, operating from a chromel-alumel thermocouple within the furnace. The furnace winding and system of resistances (Fig. 2) is similar to that employed by Norton and Fellows⁷.

Elongation of the specimen is caused by allowing sand to flow from the reservoir *D*, supported on platform scales *E*, through a glass tube into the loading bucket *F*, which is attached to the specimen by means of a steel wire. A lever may be employed when larger loads are desired. Extension of the specimen may thus be observed over a period of time under a constant load as in a creep test, or a stress-strain curve may be obtained.

Although the mirror type of extensometer is more sensitive, it was decided to observe the extension of the specimen with the aid of microscopes, because the attachment of any mechanical device to the soft metal single crystal might cause serious deformation, and because the transmission of a minute amount of extension to mirrors outside of the temperature-controlling unit might involve unknown errors. The novel feature of this microscope extensometer is that a triple lens system (Fig. 3) is employed, giving greater sensitivity and accuracy with the same working distance from objective to specimen. The sensitivity of the observations in inches of elongation per inch of length of specimen is also increased by using a long (6-in.) gage length between the fiducial marks (XX, Fig. 2), drawn on the surface of the specimen with a razor blade.

Details of the construction of the extensometer are shown in Fig. 2. The microscopes are carried on two aluminum brackets *GG* clamped to a steel sleeve *H*. The sleeve moves vertically and rotates on the main support *I*, a steel shaft 2 in. in diameter. This shaft is adjusted and

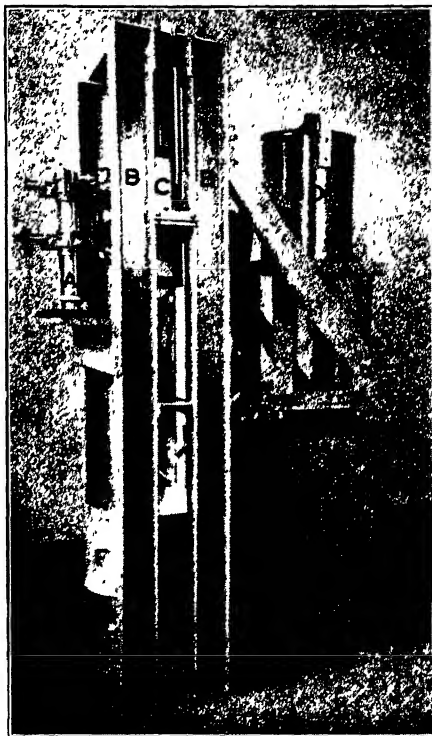


FIG. 1.—GENERAL VIEW OF CREEP-TESTING APPARATUS.

A, extensometer. *B*, supporting framework. *C*, heating furnace. *D*, sand reservoir. *E*, Toledo scales. *F*, bucket, hanging from specimen.

clamped in a vertical position by means of three supporting screws in the base.

The sleeve carrying the microscopes is moved up and down to keep the cross-hair in the upper microscope focused on the upper fiducial

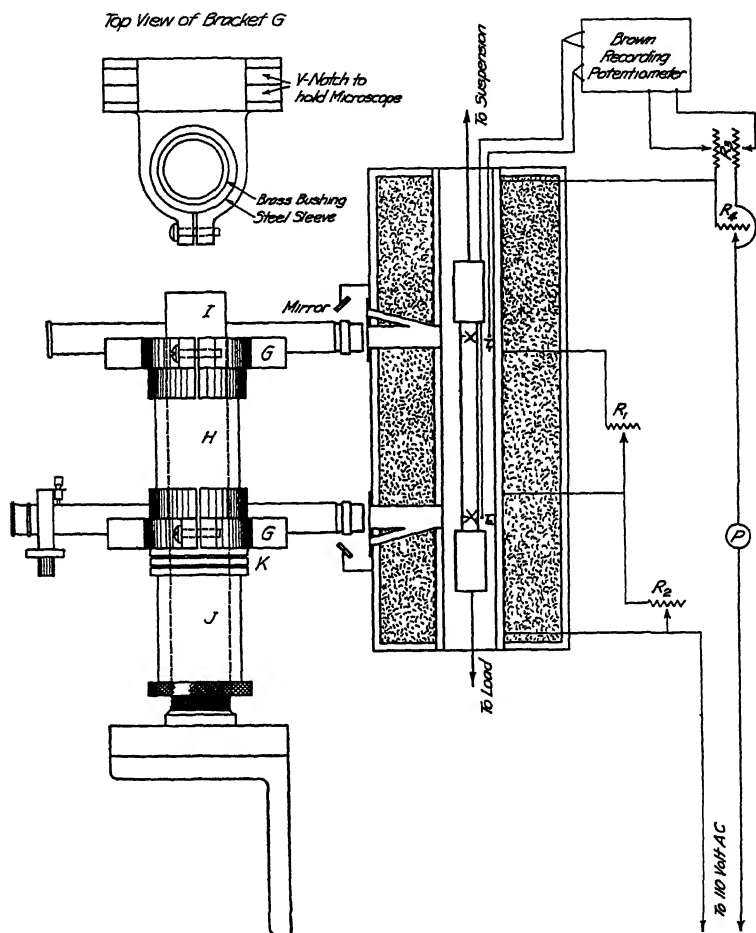


FIG. 2.—DIAGRAM OF EXTENSOMETER, ILLUMINATION OF FIDUCIAL MARKS AND SYSTEM FOR CONTROL OF TEMPERATURE.

mark of the specimen; thus preventing the error that might occur if motion took place in the grip or suspending mechanism. A 36 pitch thread is machined on the bottom of the main supporting shaft, and the collar *J*, which operates on this thread, presses against the ball bearings *K* at the base of the sleeve carrying the microscopes; thus, rotation of the screw collar *J* raises or lowers both microscopes simultaneously.

The motion of the lower fiducial mark of the specimen is measured by a screw micrometer eyepiece in the lower microscope. An over-all extension of 1 mm. can be observed without resetting.

The distance between the microscopes, and thus the original gage length of the specimen, is measured by rotating the microscopes until they are focused on two lines inscribed on the polished surface of a fused quartz rod, which is mounted parallel to the specimen on the same shelf as the extensometer.

The distance between the two lines on the quartz rod is 152.416 mm. ± 0.001 mm. measured at 70° F. from a Bureau of Standards scale. When a series of readings is being taken of the creep of a specimen, continued observations of the length of the quartz will disclose the amount of thermal expansion or contraction taking place in the sleeve

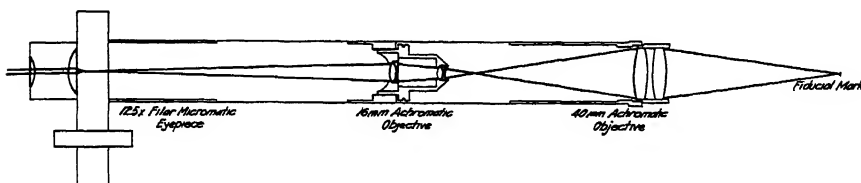


FIG. 3.—LENS SYSTEM IN MICROSCOPES AND PATH OF RAYS FROM FIDUCIAL MARK TO EYE.

separating the microscopes. By adding or subtracting the apparent change in length of the quartz, the correct length of the specimen may be obtained, and thermal errors in the extensometer may be reduced to negligible proportions.

The lens system and path of rays is shown in Fig. 3. A Gaertner 40-mm. double convex achromatic lens with numerical aperture of 0.25 is placed at a distance of 80 mm. from the specimen, forming a real image at a like distance behind. This real image is placed at the front focal plane of a 16-mm. Bausch and Lomb achromatic objective of a normal microscope system, employing a 12.5 \times Bausch and Lomb filar micrometer eyepiece and a mechanical tube length of 160 mm. This arrangement results in high magnifying power (about 125 \times) and thus high sensitivity without unduly increasing the tube length, while at the same time giving a long working distance (about 3 in.) allowing control of the specimen temperature.

Calibrated from a 0.01-mm. Leitz stage micrometer, the intervals on the drum head of the filar micrometer eyepiece represent 1.02 microns (4×10^{-5} in.). With a clear fiducial mark, it is readily possible to reproduce readings to within $\pm \frac{1}{2}$ interval. As a 6-in. gage length is employed, an accuracy of $\pm 3.3 \times 10^{-6}$ in. per inch is thus obtained.

The fiducial marks are illuminated by light from a 150-watt electric light bulb, reflected down oblique illuminating tubes by means of the focusing mirrors shown in Fig. 2.

PRODUCTION OF SPECIMENS

The zinc single crystals were cylindrical in form, 0.445 to 0.495 in in diameter by 8 to 10 in. long. They were produced by a modification of the Bridgman⁸ method from C.P. zinc (99.999+ per cent Zn) supplied by the New Jersey Zinc Co., through whose courtesy spectrographic analyses were also obtained. The major impurities in the original material were: iron, 0.0003 per cent; lead, less than 0.0002 per cent; cadmium, less than 0.00005 per cent; impurities in the single crystals, iron ± 0.0001 per cent, lead less than 0.0002 per cent, cadmium 0.00005 per cent. Considerable care was taken to insure sound castings, free from surface defects and internal gas pockets or contamination. The zinc was melted and degassed in a vacuum. The vacuum hose was then transferred to the upper end of a Pyrex glass mold, which had been thoroughly cleaned and washed with colloidal graphite to prevent sticking of the zinc. The mold was then inserted in the molten zinc, now exposed to the air, and application of the vacuum caused the zinc to rise slowly in the mold as far as a constriction; after solidification, the mold was sealed off just above this point, and withdrawn from the molten zinc bath. The solid polycrystalline castings in their glass molds were packed in Sil-O-Cel into a large test-tube, and lowered through an electric furnace at the rate of $\frac{1}{4}$ in. per hour. The polycrystalline castings melted, and then solidified gradually in the form of single crystals.

DETERMINATION OF ORIENTATION

In zinc crystals having the angle α between the basal plane and the axis of the specimen greater than about 20° , it was possible to determine the position of the c axis within $\pm 0.5^\circ$ by measurement with a contact goniometer after cleavage at the temperature of liquid air. The a axis directions were obtained by observation of the twinning directions on the basal cleavage. Such a method was of course impossible when α was less than 20° , since splitting along (0001) would destroy the cylindrical form and render the specimen useless for tensile tests. Such crystals were etched with 50 per cent HCl and the surface reflections observed with a two-circle optical reflection goniometer, in the manner described by McKeehan and Hoge.⁹ The polar angle and the azimuth of 20 reflections (two from {0001}, six from {10 $\bar{1}$ 0}, and twelve from {10 $\bar{1}$ 2}) were obtained and plotted on a stereographic projection, suitable rotation giving the desired angles.

APPEARANCE OF PLASTIC DEFORMATION

In specimens where α was greater than about 10° , a large amount of basal glide was found to precede the twinning. The crystals were there-

fore divided into two classes; the "twinning" crystals (x less than 10°), and the "ductile" crystals (x greater than 10°). No study was made of stresses or crystal mechanics of twinning on $(10\bar{1}2)$ in the ductile crystals, since this subject has been thoroughly covered by Schmid¹⁰. As might be expected from a random orientation of the original nucleus, out of 60 single crystals produced only 8 had x less than 10° . No survey of creep or the effects of temperature could be made on the twinning crystals because of the limited number, but interesting observations were made on the mechanics of deformation and fracture. These will be discussed subsequently.

Most surprising results were encountered when creep tests were attempted on the ductile zinc single crystals. Many were so ductile at

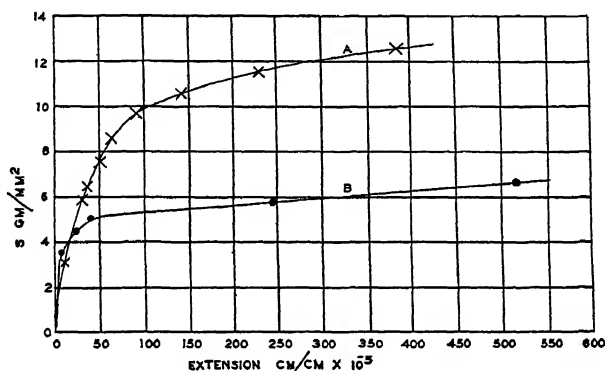


FIG. 4.—STRESS-STRAIN CURVES OF DUCTILE ZINC SINGLE CRYSTALS.

Curve A, specimen R-20, was obtained at 20°C . with load increasing at a rate of 317 grams per minute. Curve B, specimen R-12, was obtained at 200°C . with load increasing at a rate of 181 grams per minute. S is the resolved shearing stress.

room temperature that when held at one end they would droop under their own weight. When held in the middle, the most ductile would droop at both ends. Since it seemed quite possible that at room temperature zinc is above the critical temperature (T_d), claimed by Taylor⁶ as necessary for a finite critical shearing stress, ductile crystals were cooled to 0°C ., -75°C . and -175°C . At each successive temperature, the crystals were found to remain ductile and to deform under their own weight. Indeed, after being straightened out they would droop again while still at the low temperatures. (It should be noted here that the shearing stresses introduced in bending were somewhat larger than the shearing stresses caused by tension in the creep tests.) As shown by Schmid¹⁰ in his studies of the "short-time" elastic limit, temperature seems to have little effect on the critical shearing stress.

The crystallographic nature of the creep was demonstrated by the fact that the loads necessary to produce similar creep rates in different specimens varied with x , the most ductile having x about 45° . Stress-

strain curves of the ductile crystals showed the appearance of plastic deformation with shearing stresses of less than 3.5 grams per sq. mm. (Fig. 4). Even smaller stresses were found to cause continued extension when the crystals were examined under creep conditions. Continuous extension took place at 200° C. with an applied shearing stress of less than 2.6 grams per sq. mm. (3.7 lb. per sq. in.)* (Fig. 5) and at 25° C., with a shearing stress of less than 2.8 grams per sq. mm.; these are very close to the smallest shearing stress that could be applied in tension with the apparatus used (about 1.3 grams per sq. mm. produced by the force of gravity on the specimen and grip). The data concerning the crystals in Figs. 4 and 5 are given in Table 1.

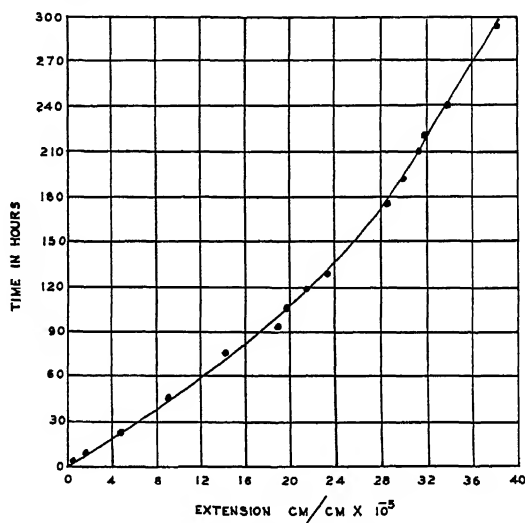


FIG. 5.—CREEP OF DUCTILE ZINC SINGLE CRYSTAL NO. R-13 AT 200° C. CAUSED BY A RESOLVED SHEARING STRESS OF 2.6 GRAMS PER SQUARE MILLIMETER.

The first visible trace of plastic deformation in the ductile crystals was the appearance of quite uniformly distributed elliptical lines, marking the intersection of the basal glide planes with the surface of the specimen. Simultaneously with the appearance of these glide ellipses, one or two sharply defined elliptical lines generally appeared (Figs. 6 and 7) cutting across the former set and making an angle of $90^\circ - \frac{x - x'}{2}$ with the basal glide planes, where x and x' are the initial and final angles between the basal planes and the axis of the specimen. Upon close examination, it appeared that this latter line cutting across the glide ellipses represented a stage in the flexural gliding process, the significance of which was not

* Data available in this field have been expressed in terms of grams per square millimeter, which is close to the figure commonly used in American engineering practice. (Conversion factor, 1 gram per sq. mm. = 1.42 lb. per sq. in.)

TABLE 1

Specimen	α	λ	ψ	ξ	Diameter, In	Twin Load, Lb	T , Grams per Sq. Mm.	T' Grams per Sq. Mm	ϕ	ϕ'
R-45	0 5°	13°	44 5°	50°	0 445	299	613	642	73°	74°
A-11	1 7		44 0	47	0 483	240	438	454	78	76
R-44	1 0	2 5	41 0	54	0 457	250	414	441	62	62
R-46	4 0	26 5	43 0	43	0 485	210	400	427	84	84.2
R-38	3 0	13 0	45 5	53	0 450	210	398	416	74	68
R-34	4 0	9 0	46 0	55	0 455	220	392	413	67	67 5
R-33	8 0	12 0	41 0	65	0 445	150	320	335	69	69
A-61	9 0		37 5	38	0 467	200	312	314		76 5
R-2	73 0	73 0			0 480					
R-12	28 7	29 2			0 503					
R-20	66 5	66 6			0.495					
R-13	30 0	37 8			0 488					

α angle between axis of specimen and {0001} glide plane.

λ angle between axis of specimen and glide direction [11 $\bar{2}$ 0].

ψ angle between axis of specimen and twinning plane {10 $\bar{1}$ 2}.

ξ angle between axis of specimen and twinning direction (trace of {1 $\bar{2}$ 10} on {10 $\bar{1}$ 2}).

ϕ angle between axis of specimen and prismatic fracture, calculated.

ϕ' angle between axis of specimen and prismatic fracture, observed.

T , twinning stress, calculated from original cross section.

T' , twinning stress, calculated from final cross section.

noted by Schmid¹¹ in his original work. In slipping from their original to their final position, the basal glide planes seemed to go through a sharp bend (Figs. 6 and 7) having close similarity to the twinning boundary shown by Andrade¹² for mercury. It is the plane joining these bends, hereafter called the "bend-plane," that gives the second elliptical line on the surface of the crystal, cutting across the glide ellipses at the start of the deformation. The idea immediately suggests itself that the bend-plane is a twin boundary, the zinc crystal on one side of the bend-plane, or twin plane, being a mirror reflection of the crystal on the other side of the bend-plane. This type of twinning is distinct from that usually considered to take place in zinc, which is confined to the first order pyramidal

planes $\{10\bar{1}2\}$ as shown by Mathewson¹³, since the bend-plane makes an angle¹⁴ of $90^\circ - \frac{x + x'}{2}$ with the axis of the specimen, and an angle of $90^\circ - \frac{x - x'}{2}$ with (0001). The angle between (0001) and the bend-plane is thus a variable, dependent on the amount of deformation.



FIG. 6.—ELONGATED DUCTILE ZINC SINGLE CRYSTAL, SHOWING OCCURRENCE OF "TWINNING" BOUNDARY DURING BASAL GLIDE.

Cleavages along (0001) made after chilling to the temperature of liquid air reveal further information concerning the possible crystallographic significance of the bend-plane (Figs. 8 and 9). The basal cleavage is seen to possess, beside the $\{10\bar{1}2\}$ twins, a second set of lines making an angle of 30° with the first set. Their similarity to the $\{10\bar{1}2\}$ twins is marked. If the basal cleavage is examined in the region of the bend, it is seen that the intersection of the bend-plane with the basal plane is parallel to one of the sets of secondary twins mentioned above (Fig. 8). It may be, then, that the bend-plane represents twinning on a second order pyramidal face of variable index. The tendency of the bend-plane to assume this crystallographic relationship was checked on several specimens.



FIG. 7.—SECTION OF TRANSITION ZONE FROM ELONGATED DUCTILE ZINC SINGLE CRYSTAL, CLEAVED PARALLEL TO THE BASAL PLANES, SHOWING SHARPLY DEFINED "TWINNING" OR "BEND" PLANE.

Examination of a basal cleavage section from a strongly deformed crystal shows it to be covered with the secondary twin striae (Fig. 9), while the undeformed cleavage sections show few or none. This development of secondary twins during the flexural gliding process may help to account for the phenomenon of shear strengthening.

The development of the transition zone and bend-plane during the extension of the ductile crystals may explain the course of the creep curve, which assumes an S-shape if the test is prolonged (Fig. 10). The first rather rapid extension probably corresponds to the phase of pure

translation; the creep rate then slows up, due perhaps to the initiation of second order twinning and bending in the transition zones. The creep then increases to a steady rate, due to the development and extension of the band.

Deformation is uniform over the entire gage length only during the first small amount of extension, but even in this section of the curve the creep rate is steadily changing. For this reason, no one creep rate could be considered as characteristic of a particular shearing stress in an individual crystal, and only a qualitative comparison could be made between different specimens. The slowest creep studied was with a resolved shearing stress of 2.6 grams per sq. mm. at 200° C., and with a shearing stress of 2.8 grams per sq. mm. at 25° C., showing that the threshold shearing stress is less than these values at these temperatures.



FIG. 8.—BASAL CLEAVAGE SECTION FROM TRANSITION ZONE.

The sharp white line marks intersection of "bend" plane with basal plane. Although appearing as a flat plate in the photograph, the section of the basal plane above the white line is sharply bent away from the lower section. The parallelism of the bend line and the secondary twin striae is clearly shown.

OBSERVATIONS ON TWINNING CRYSTALS (x less than 10°)

As mentioned above, it was desired to examine crystals in which twinning was preceded by little or no basal glide. Unfortunately, the small number of such crystals and the limited time available prevented their study under creep conditions.



FIG. 9.—BASAL CLEAVAGE SHOWING FIRST-ORDER AND SECOND-ORDER TWINS.

The eight specimens were tested in a Baldwin-Southwark hydraulic tensile testing machine. Results are shown in Table 1. The load at which the first twin appeared was determined by the coincidence of a sudden decrease of load and the occurrence of the characteristic snapping sound of twinning. The twinning stress T resolved as a shear along $\{10\bar{1}2\}$ and in the direction of

twinning (trace of the second-order prism face $\{1\bar{2}10\}$ on twinning plane $\{10\bar{1}2\}$) is given by Dawidenkov¹⁵ as

$$T = P \sin \psi \cos \xi$$

where P is the average tensile stress, ψ is the angle between the axis of the specimen and the twinning plane (the $\{10\bar{1}2\}$ plane on which the resolved shearing stress is a maximum), and ξ is the angle between the axis of the specimen and the twinning direction. The twinning stresses are similar to those found by Schmid¹⁰ for cadmium (512 grams per sq. mm.).

Since the conclusions reached in the earlier part of the paper suggest that twinning stresses obtained by rapid testing might be higher than those that would be obtained if the tests were carried out under creep conditions, several twinning specimens were examined in the creep-testing

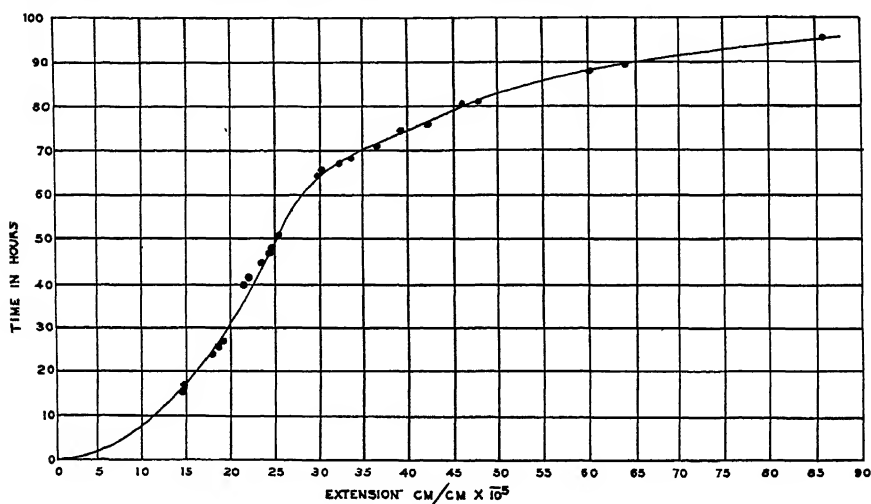


FIG. 10.—CREEP OF DUCTILE ZINC SINGLE CRYSTAL No. R-2, AT 25° C. CAUSED BY RESOLVED SHEARING STRESS OF 8.0 GRAMS PER SQUARE MILLIMETER.

machine, under slow application of load. They all showed some creep due to basal glide, but no twinning even after considerable durations of loads as high as those that produced twinning in the hydraulic testing machine.

It will be noted from Table 1 that there is a wide variation in the stress necessary to produce twinning, and that this stress is higher the smaller the angle α (Fig. 11). Thus it appears that the larger the amount of basal glide preceding twinning, the lower the twinning stress.

Evidence has been shown by Elam³ and others that glide on one set of slip planes in a single crystal may strengthen another potential slip plane against shear, but no evidence or explanation is known for the lessening of a shear stress by preceding deformation on another plane. It was at first thought that this phenomenon might be only apparent, and actually

due to a decrease of the cross section of the specimen by the preceding basal glide, since the twinning stresses were calculated on the basis of

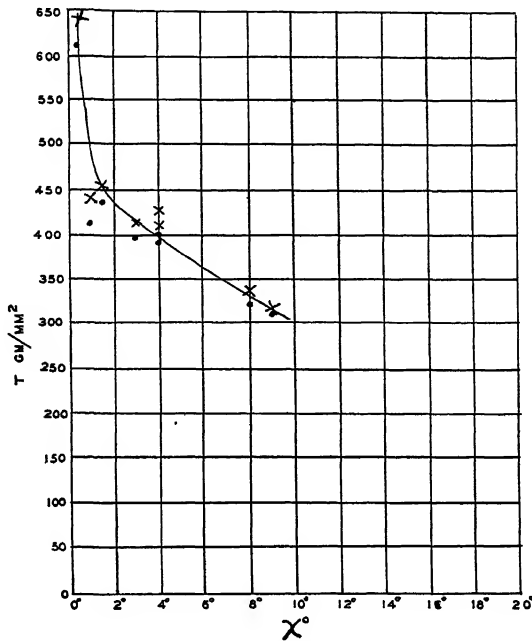


FIG. 11.—CURVE SHOWING THAT THRESHOLD TWINNING STRESS T IS INVERSELY PROPORTIONAL TO AMOUNT OF PRECEDING BASAL GLIDE.

α is the angle between the basal plane and the axis of the specimen. Values marked by dots are calculated on the basis of the original cross section, and values marked by crosses are calculated from the final cross section.



FIG. 12.—TWINNING AND FRACTURE IN ZINC CRYSTAL HAVING BASAL PLANE NEARLY PARALLEL TO SPECIMEN AXIS.

the original cross section. However, the twinning stresses were recalculated on the basis of the decreased cross section (T' , Table 1, values

shown by crosses in Fig. 11), and the slope of the curve is only made more apparent.

The conclusion that the critical stress necessary for twinning is very much larger than the critical stress for glide is not so surprising when the difference in the crystal deformation process is considered. Taylor⁶

clearly excludes twinning from his theory of low critical stresses, since he states:

The fact that the macroscopic distortion of metallic crystals is a shear parallel to a crystal plane and in a crystal direction, and the fact that this remains true even when the distortion is large, shows that the plastic strain must be chiefly due to the sliding of one plane of atoms over its immediate neighbor in such a way that the perfect crystal structure is reformed after each atomic jump.

Before each twinning test, a complete stereographic projection was made of the principal planes of the crystal under examination, and their angular relationship to the axis of the specimen was determined. The first-order pyramidal plane $\{10\bar{1}2\}$ having the angle ψ nearest to 45° was selected as the one on which twinning was most likely to occur. Since two $\{10\bar{1}2\}$ planes in the same zone make an angle¹³ of 87° with one another, if one plane makes an angle of about 45° with the axis of the specimen, it was predicted and found that the other pyramidal plane $\{10\bar{1}2\}$ in the same zone would also make an angle of approximately 45° with the axis of the specimen, and twin almost as readily (Fig. 12).

Fracture took place in a manner similar to that first described by Mathewson¹³. It occurred on



FIG. 13.—RECRYSTALLIZATION IN ZINC SINGLE CRYSTAL. This specimen was tested for threshold twinning stress at 200°C ; basal plane was originally almost parallel to specimen axis.

the new basal planes of the twins—on the first-order prismatic face $\{10\bar{1}0\}$ in the same zone as the two pyramidal planes figuring in the twinning (Fig. 12). The angle ϕ between the surface of fracture and

the axis of the specimen, predicted from the stereographic projection, agreed closely with the observed angle ϕ' (Table 1).

One heavily twinned crystal was found to have recrystallized on cooling from 200° C. Two sets of crystallites appeared (Fig. 13). They had a marked preferred orientation, evidently being related in orientation and origin to the two major sets of twin bands. The appearance of the specimen was similar to the recrystallized cadmium crystal shown by Schmid².

CONCLUSION

The results of the present work demonstrate the value of creep tests in revealing the limits of the elastic range. There appeared to be no measurable critical shearing stress or elastic limit in ductile zinc single crystals when tested in creep at or above room temperature. Definite evidence was found of plastic deformation with the smallest shearing stresses that could be applied, in harmony with the requirements of Taylor's⁶ theory of crystal deformation. No indication was observed of a critical (or recrystallization) temperature (T_d) below which a much larger critical shearing stress might occur; indeed, a remarkable degree of ductility was maintained by the crystals at the temperature of liquid air.

Flexural gliding was found to involve a new type of twinning on second-order pyramidal planes.

There appeared to be a large, definite threshold stress for twinning on $\{10\bar{1}2\}$, which varied inversely with the amount of preceding basal glide. This observation may help to explain the difficulty of previous investigators in obtaining a constant twinning stress at any one temperature.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the Department of Metallurgy of Yale University for the opportunity for carrying out this research project, and particularly to Dr. C. H. Mathewson, of Yale, and Dr. R. F. Mehl, of Carnegie Institute of Technology, for their invaluable suggestions and criticisms.

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DISCUSSION

(J. G. Thompson presiding)

C. H. MATHEWSON,* New Haven, Conn. (written discussion).—In regard to the second order twinning which takes place during basal glide, it is evident that the parts of the crystal are brought into a 180° rotation twin relationship by movements of translation not occurring on the twinning or composition plane, and the movements are, therefore, quite different from those occurring in the well-known process of mechanical twinning by shear from plane to plane in an amount less than the distance between atoms on the twinning plane. It is significant that the critical angle varies with the amount of plastic deformation and the orientation at any stage of the process.

L. W. MCKEEHAN,† New Haven, Conn.—The question of the reduced shearing stress necessary for twinning after basal glide has started bothers me a little, and one possible way of thinking of it has occurred to me. The greater the amount of basal glide and, therefore, in terms of angle, the greater the angle the basal plane makes with the axis, the wider we may suppose the zone of disturbed material to be on each side of the geometrical plane including the first failure.

In that zone there is a certain amount of disturbance of the structure, which can be described in all sorts of ways. One way is to say the planes are bent. If they are bent, they are bent principally about lines in that plane. Of course, the necessary condition for the formation of twins is the presence of material with basal planes inclined to the original basal planes, at something around 45°. Therefore it seems quite possible that after a certain amount of deformation, we are more likely, in materials where the basal plane makes a large angle with the axis, to find nuclei for twin formation and, therefore, the stress necessary to initiate twinning will be diminished.

It will be observed, too, that these twins can proceed to the boundary if most of the deformation has occurred along one plane in the crystal, without striking any material to hinder their progress. In other words, the hindrance of slip on a plane intersecting the first plane of slip is not here involved. This process can produce

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twins on both sides of the original plane of deformation, and increase the length of the specimen thereby, without encountering such interference.

M. GENSAMER, * Pittsburgh, Pa.—We are attempting to do the same sort of thing with single crystals of iron, feeling as Dr. Miller does about critical shearing stresses for slip. We cannot say much about our results at this time, but it does seem as though our crystals of iron, of decarburized mild steel, have a definite critical shearing stress for slip. At least, we have had a considerable load on one single crystal and it has not slipped yet. So, in other metals than zinc, perhaps there are yield points.

Was the amount of rotation accompanying translation sufficient to account for the diminishing resistance to twinning as translation proceeded? Was the amount of extension enough so that there was a sufficient amount of rotation of the crystal? What I have in mind is this: an unstrained crystal of a certain orientation might slip rather than twin, whereas another crystal, which had arrived at the same orientation by the rotation accompanying slip, would be harder and might twin rather than slip. This depends, of course, on whether or not there was enough rotation to produce the effect and on how much extension there was.

I want to ask a question about the other kind of twinning. I have not thought enough about it to be sure that what I am going to ask has any sense, but might this be a case of what Schmid (I do not remember who established the nomenclature) calls twinning of the second kind, in which the composition or twinning plane is not a plane of rational crystal indices, but only the twinning direction has crystallographic significance? I believe that kind has been observed in crystals, not metals, of low degree of symmetry.

It might have been very useful if Dr. Miller had been able to estimate the volume of each twin as it was formed. It has been suggested that the elastic energy necessary to produce mechanical twinning is affected by the size of the region that eventually twins; if true, this might lead to the effect observed by Dr. Miller, provided the width of twin bands diminished as translation proceeded.

R. F. MILLER (written discussion).—In answering Dr. Gensamer, it should be stated that in subsequent work on aluminum, silver and zinc single crystals, it appears that a definite critical shearing stress may be encountered above the lowest temperature of recrystallization for the metal being considered. In regard to the second question, the amount of glide preceding the twinning was very slight, certainly not enough to rotate the glide planes of different crystals into similar positions. As to the third point, the author has not had the opportunity to examine the similarity between the second-order twinning in zinc single crystals and Schmid's "twinning of the second kind." The volume of the twins could not be estimated as they formed, since once the critical twinning stress was exceeded, a large number of twin bands of approximately the same volume formed almost simultaneously throughout the length of the crystal.

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An Investigation of the Zinc-rich Portion of the System Iron-zinc

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MEMBER A.I.M.E.

(Chicago Meeting, October, 1935)

IN recent years various problems in connection with research work on the preparation and properties of zinc-base alloys have required reliable information concerning the constitution of the zinc-rich portion of the iron-zinc equilibrium diagram. On numerous occasions rather positive indications were obtained that, for example, the solubility of iron in zinc was incorrectly represented on the current equilibrium diagrams. A careful study of all the available literature relating to the iron-zinc system led to the conclusion that much of the early work was unsatisfactory as measured by present standards of experimental accuracy, and as a result it was decided to redetermine the location of the liquidus curve and of adjacent portions of the diagram.

Part I of this paper comprises a description of the experimental methods and a summary of the results by means of which the zinc-rich end of the iron-zinc diagram has been revised in the following ways:

1. Measurements of the solubility of iron in liquid zinc by several different sampling methods, leading to a relocation of the liquidus curve.

2. Microscopic, conductivity, and X-ray studies of the solid solubility of iron in zinc, which, together with thermal analyses, have resulted in new values for the solid solubility and the eutectic temperature and composition.

3. Heating and cooling curves, obtained by a refined differential method, leading to new locations for the two peritectic horizontals.

In Part II of the paper the attempt is made to review all of the published work having a bearing on the constitution of the iron-zinc system, and to correlate the present results, and some recently published data involving the use of X-ray technique, with the earlier work, much of which was done from 25 to 30 years ago.

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PART I.—EXPERIMENTAL

MEASUREMENTS OF LIQUID SOLUBILITY

In all of the early work on the iron-zinc system, the liquidus curve was located by obtaining primary cooling-curve arrests. A study of the original papers, however, has led to the conclusion that in many cases the composition of the synthetic alloys was not correctly given because all of the iron was probably not in solution when the cooling curves were taken. Attempts in this laboratory to obtain such primary arrests by a refined differential method have failed to give positive results. Finally, the thermal arrest method is not fundamentally an equilibrium method.

For these reasons it was decided to employ direct sampling, by more than one method, of a series of melts in equilibrium with excess iron over the temperature range from the melting point to the boiling point of zinc. These solubility measurements were carried out at different times by different investigators, two methods of sampling the melt being used in the temperature range from 425° to 650°¹, and a third method

in the range from 675° to 875°; in addition, a few experiments were made by one of the first methods in the higher temperature range. The results obtained by each method will be discussed separately. The liquidus curve obtained by plotting the combined data on a large scale is shown in Fig. 1.

The materials used were Horse Head Special zinc and Armco iron sheet. The zinc is specified to be 99.99+ per cent pure. That used in the work in the lower temperature range was not further analyzed; that used in the higher temperature range was analyzed spectroscopically and

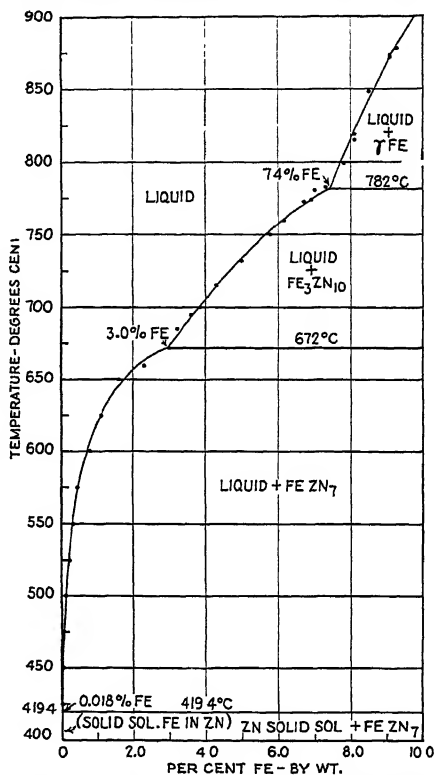


FIG. 1.—SOLUBILITY OF IRON IN MOLTEN ZINC.

¹ All temperatures given in this paper are in degrees Centigrade.

found to contain the following percentages of impurities: Pb, 0.001; Fe, 0.0011; Cd, 0.002; and, if present, Cu less than 0.0005; and Sn, less than 0.0013. The Armco iron was not completely analyzed, but the manufacturers very kindly supplied us with a typical analysis² of the impurities in Armco iron sheet, as follows: C, 0.012 per cent; Mn, 0.018; P, 0.004; S, 0.022; Cu, 0.044; Si, trace.

Tube Method, 425° to 650°

A small Pyrex tube holding about 300 grams of metal was supplied with a closed side arm near the top, and was mounted in a refractory base. The required amount of molten metal or alloy was then added and covered with graphite powder, and the tube was inserted in a large muffle-type furnace and kept at a controlled temperature until equilibrium had been attained and the zinc was saturated with iron³. At temperatures up to 525° the metals were added in the form of an iron-zinc alloy containing a known excess of iron; at the remaining temperatures the iron was added in the form of fresh turnings.

At the conclusion of an experiment, the furnace was opened and a sample obtained as quickly as possible to prevent any serious change of temperature. The sample was obtained by breaking the side tube, discarding the first few drops of metal that flowed out, and collecting the remainder (about 40 grams) in a small porcelain crucible. The entire sample was analyzed for iron. The experimental conditions and analytical results are given in Table 1.

The large furnace used was controlled by a Leeds & Northrup temperature controller, and it is believed that the sample and the adjacent calibrated chromel-alumel thermocouple, in the middle of the furnace, did not change in temperature more than $\pm 2^\circ$ throughout an experiment.

Ladle Method, 450° to 660°

In this method a melt was prepared by maintaining a crucible containing about 6 lb. of zinc and the required excess of iron at an elevated temperature until all the iron was in solution. The temperature was then lowered slowly to that at which it was desired to sample the melt, and maintained at that temperature for an hour in a covered crucible-type resistance furnace. After a sample had been taken, the temperature was

² This analysis was supplied through the kindness of Mr. R. F. Passano, of the American Rolling Mills Co., Middletown, Ohio.

³ Actually the experiments were performed in the reverse order to that given in Table 1, so that some idea of the length of time required to reach equilibrium was first obtained at the higher temperatures. The experiments of longer duration were done first at each temperature. When a previously prepared alloy was used, shorter heating times could usually be used.

lowered to the next sampling temperature and held there for an hour, then another sample was taken. Thus a series of samples was obtained in which the equilibrium temperature was approached from above. A similar series of samples was obtained by approaching the sampling temperature from below. Stirring of the melt was not employed.

TABLE 1.—*Summary of Experimental Data for Tube Method*

Temperature, Deg. C.	Experiment No.	Time, Hr.	Fe	
			Per Cent	Average Per Cent
425	1	140	0.016	
425	2	240	0.022	0.020
425	3	240	0.022	
425	4	240	0.021	
450	1	41	0.032	
450	2	41	0.030	0.031
475	1	26	0.061	
475	2	28	0.05	0.056
525	1	28	0.25	
525	2	28	0.21	0.23
550	1	48	0.38	
550	2	96	0.32	0.33
550	3	144	0.28	
575	1	23	0.45	
575	2	139	0.43	0.44
600	1	168	0.72	
600	2	168	0.82	0.77
625	1	77	1.0	
625	2	125	0.98	1.0
650	1	96	1.5	
650	2	120	1.7	1.6

Samples were obtained by means of a small preheated silica ladle. The entire liquid sample was quickly water-poured and the entire sample, approximately 50 grams, was analyzed for iron.

Three different alloys were used, containing, respectively, 0.5, 5.0 and 8.0 per cent iron, each alloy being used in an appropriate temperature range, to provide excess iron and yet avoid too large an amount of solid material. Furnace temperatures were adjusted manually, and were read by means of a calibrated chromel-alumel thermocouple. It is thought

that the recorded temperatures were accurate to $\pm 5^\circ$. Duplicate experimental results were obtained up to 660° . In addition, a few experiments were made at higher temperatures, but temperature control was difficult and at the time not a great deal of confidence was placed in the results. When the data from the third method became available, however, it was found that the earlier results checked well with the latter. The experimental results are given in Table 2.

TABLE 2.—*Summary of Experimental Data for Ladle Method*

Temperature, Deg. C.	Fe		
	Ascending Per Cent	Descending Per Cent	Average Per Cent
450	0.028	0.037	0.032
475		0.064	0.064
500	0.11	0.11	0.11
550	0.34	0.34	0.34
600	0.79	0.86	0.82
625	1.2		1.2
650	1.6	1.5	1.55
660	2.4	2.2	2.3
685		3.2	
700	3.9	3.8	
750		5.8	
775		6.6	

Pipette Method, 675° to 875°

In this method the required amounts of iron and zinc, totaling 350 to 500 grams, were placed in a silica-tube crucible, and when melted filled the crucible to a height of 4 or 5 in. The alloys were melted in a small vertical resistance furnace having a central heating space $1\frac{3}{4}$ in. in diameter by 19 in. long. The crucible was placed so that the center of the melt was at the center of the furnace. After the metal had melted, a salt flux (either KCl-KI or KCl-NaCl) was added to prevent oxidation of the zinc, which otherwise would be rather rapid in the temperature range employed.

The melt was stirred when necessary by means of a silica rod having a small ring at the lower end, the rod being attached at the upper end to a vacuum-type windshield wiper arranged to provide vertical agitation of the melt.

The molten alloy was allowed to stand for several days at some temperature well above the highest at which a sample was to be taken. Finally, the melt was stirred for several hours, until solution of iron was believed to be complete, as shown by probing with a silica rod. Stirring

was again begun and continued while the temperature was gradually lowered (usually 15° to 25°) to the desired sampling temperature and for from 2 to 4 hr. thereafter. The stirrer was then removed, a thermocouple in a silica protection tube was inserted so that the junction was at the middle of the melt, and the system was allowed to stand for 3 or 4 hr. at the sampling temperature. The couple was introduced very slowly into the crucible so that the couple might reach the proper temperature before coming in contact with the melt, thus avoiding the precipitation of iron on a cold couple tube.

Finally, a 1/8-in. bore silica sampling tube with a capillary tip, through which a very slow stream of hydrogen was flowing, was slowly inserted into the crucible, until the tip was about an inch below the surface of the metal. After a few bubbles of gas had escaped, to force out any flux that might have entered the tube, the latter was quickly lowered so that the tip was at the middle of the melt. After the gas had bubbled once (much bubbling would cause undesirable stirring) a three-way stopcock was turned, which shut off the flow of hydrogen and connected the sampling tube with a partly evacuated flask, thus causing a small amount of metal to be sucked up into the sampling tube. The tube was then quickly withdrawn and held until it had cooled enough to solidify the sample. Samples were usually about 4 in. long and weighed about 10 grams; they were readily removed from the sampling tube. After the sample was taken, the temperature was again read in order to make sure that the act of sampling had not lowered the temperature, and the thermocouple was then removed from the melt.

The temperature was lowered about 25° and the melt allowed to stand at the lower temperature overnight. The following morning the stirrer was inserted and the melt was stirred while the temperature was being raised to the previous sampling point and for 2 to 4 hr. thereafter. From this point on, the procedure was the same as that described above.

At least two samples were thus obtained at each temperature in the presence of excess iron, and the agreement of the analytical results indicated that equilibrium had been attained when approaching the sampling temperature from each side. Samples usually were obtained from a single melt at a series of progressively lower temperatures, seven different melts being prepared in all.

The laboratory furnace used in this work was provided with compensated windings so that a 5 or 6-in. zone could be obtained at the center of the furnace tube where the temperature was constant to within one or two degrees; with the sample in place a couple placed directly in the melt showed no variation in temperature from top to bottom of the melt.

Separate platinum-platinum rhodium couples were used to measure and control the furnace temperature, and to measure the temperature of the melt while it was being sampled. These two couples usually indi-

cated identical temperatures, and never a difference of more than one degree. They were frequently checked against two standard couples, which in turn were calibrated against the freezing points of copper, copper-silver eutectic, and aluminum, on an apparatus capable of an accuracy of 0.05° . The freezing points of these metal samples were all certified by the U.S. Bureau of Standards and, as given in the recent paper of Roeser and Wensel⁴, are as follows: copper, 1083.0° ; copper-silver eutectic (28.1 per cent copper, 71.9 per cent silver), 778.8° ; aluminum, 660.15° C., all on the International Temperature Scale⁵. Compensated connecting leads were used, and the potentiometers were calibrated at frequent intervals. Temperatures were read to within one degree, but in spite of the precautions taken it is felt that, owing to the difficulty in eliminating all errors from thermocouple temperature measurements, the temperatures reported may be in error by a maximum of 2° , referred to the fixed points mentioned above.

In the experiments with alloys 92, 93, 94 and 95 (Table 3), the furnace temperature was regulated by hand, with the result that the temperature occasionally varied two or three degrees in the course of the 4-hr. period at constant temperature. Later a Tagliabue temperature controller of the modern photoelectric cell type was obtained, which proved to be highly satisfactory. With the controller couple placed just outside the sample tube, a furnace temperature constant to $\pm 1^\circ$ could readily be attained, while a couple placed directly in the melt showed no detectable temperature variation over long periods of time.

Chemical analyses of entire samples were carried out with considerable care. Contamination by flux was less than 0.01 per cent. The samples contained from 3 to 10 per cent of iron, and it is believed that the analytical results are accurate to well within 0.1 per cent Fe.

The results obtained between 675° and 875° are given in Table 3. An attempt to obtain a sample at 665° failed because while the melt was cooling from 675° the crucible broke, probably because of the precipitation and expansion of FeZn_7 .

The solubility data given in Tables 1, 2 and 3 are plotted in Fig. 1, thus establishing the liquidus curve from the melting point of zinc up to within a few degrees of its boiling point. Wherever average values are given in the tables, these were used in plotting the curve, but without being weighted accordingly.

The liquidus curve was drawn to fit the data and at the same time to agree with the new location of the peritectic horizontals at 782° and 672° , respectively; the latter work will be discussed later in this paper. It is believed that the liquidus curve as drawn is correct to within an experi-

⁴ W. F. Roeser and H. T. Wensel: *Jnl. U.S. Bur. Stds.* (1935) **14**, 255.

⁵ G. K. Burgess: *Jnl. U.S. Bur. Stds.* (1928) **1**, 635.

mental error of 0.002 per cent Fe from 425° to 500°; 0.05 per cent Fe from 500° to 600°, and 0.1 per cent Fe from 675° up to 875°.

A single experiment was performed at 795°, in which a silica-tube crucible was provided with a vertical partition so that the 25-gram sample of Armco iron could be kept separate from the main body of molten zinc, the latter becoming saturated with iron only by diffusion over the partition. After standing at 795° for 382 hr. the metal on each side of the partition was sampled separately by breaking sealed outlet tubes and draining off first the zinc side, then the iron side. The liquid from the latter contained 7.5 per cent Fe, in good agreement with results obtained by the pipette method, while the liquid from the former contained only 3.4 per cent Fe.

TABLE 3.—*Summary of Solubility Data by the Pipette Method*

Alloy No.	Sample No.	Sampling Temperature, Deg. C. Approached from		Fe		Average Temperature, Deg. C.
		Above	Below	Per Cent	Average Per Cent	
93	1	877		9.4		
93	2	877		9.2		
93	3		877	9.3	9.3	877
93	4		877	9.3		
92	1	870		9.2		
92	2	872		9.1	9.1	871
92	4		871	9.0		
108	1	872		9.1		
108	2		872	9.1	9.1	872
94	11	849		8.5		
94	12		846	8.5	8.5	847
94	13		846	8.4		
94	5	814		8.3		
94	6	813		7.9	8.1	814
94	8		818	8.1		
94	9		818	8.0	8.05	818
105	1	798		7.8		
105	2		798	7.8	7.8	798
95	1	780		7.0		
95	2	780		6.9	6.95	780
95	5		782	7.3		
95	6		782	7.3	7.3	782
95	13	773		6.9		
95	14	773		6.9		
95	11		772	6.8	6.85	
95	12		772	6.8		772
105	3	759		6.2		
105	4		759	6.1	6.15	759
105	5	730		4.9		
105	6		731	5.0	4.95	730
106	1	714		4.3		
106	2		715	4.3	4.3	714
106	3	695		3.6		
106	4		694	3.6	3.6	694
106	5	672		3.0		
106	6		672	3.0	3.0	672

Diffusion of iron in molten zinc is thus seen to be slow, and this experiment is additional proof that a long time must be allowed for saturation of zinc with iron, unless stirring is employed. This is one of several experiences that have led the authors to conclude that the experimental conditions used by the early workers on the system made impossible complete saturation of zinc by iron.

Table 4 shows the solubility of iron in zinc as read from the original large-scale curve from which Fig. 1 was prepared. Values are given for each 25° from 425° to 900°, and at the eutectic and the two peritectic temperatures. A general comparison of these results with previously published data may be made by saying that the solubility of iron in zinc, expressed in weight per cent, has been found to be about 1 per cent lower at 675°, about 4 per cent lower at 775°, and about 8 per cent lower at 875° than is indicated by the earlier data.

TABLE 4.—*Solubility of Iron in Molten Zinc*

Temperature, Deg. C.	Fe, Per Cent	Temperature, Deg. C.	Fe, Per Cent
419 4	0.018	675	3.05
425	0 02	700	3.85
450	0.03	725	4 65
475	0.06	750	5 65
500	0.10	775	6.95
525	0.20	782	7.40
550	0.30	800	7.70
575	0.45	825	8.15
600	0.70	850	8.65
625	1.10	875	9.15
650	1.75	(900)	(9 75)
672	3.0		

THERMAL ANALYSIS

Thermal arrests obtained by means of heating and cooling curves were used to redetermine the eutectic and the two peritectic temperatures.

The furnace in which these results were obtained was connected to a specially built, synchronous motor-driven rheostat, so arranged that several rates of heating or cooling could be obtained⁶. The sample, contained in either a Pyrex or a silica tube, was packed into a graphite crucible with graphite powder. Differential temperature measurements were employed, one thermocouple being fitted into a groove on the outer surface of the graphite crucible to measure the furnace temperature, and the other being immersed directly in the sample to a point about $\frac{3}{8}$ in. from the bottom of the tube. The thermocouple circuits were operated

⁶ It is expected that a description of this entire apparatus for thermal analysis will be available in a forthcoming publication.

by means of oil-immersed switches driven by the same motor that controlled the rheostat. By means of a time signal device, readings on one couple were taken every minute and half minute, and on the other couple every quarter and three-quarters minute.

Thermocouple readings were obtained by means of a White potentiometer in conjunction with sensitive wall galvanometers. Iron-Constantan couples were used in obtaining the eutectic arrests and for a few of the lower peritectic arrests; chromel-alumel couples were used for most of the work at the two peritectic temperatures. The couples were carefully annealed when made, and were calibrated before and after each experiment against the pure metal standards previously mentioned, together with a sample of pure zinc certified by the U.S. Bureau of Standards to freeze at 419.45° .

Eutectic Arrest

The alloys were prepared from Armco iron and a special lot of zinc, which had the following spectroscopic analysis, in per cent: 0.0009 Fe, less than 0.0002 Pb, less than 0.00015 Sn, less than 0.00005 Cd, and 0.000008 As. The alloys were made by direct addition of iron to the molten zinc, which was heated in a graphite crucible until solution of the iron was complete; then each alloy was cast into a 4 by $\frac{3}{4}$ -in. dia. cast-iron mold. One such casting constituted a sample for thermal analysis, and was remelted in a Pyrex-lined graphite crucible in the special furnace.

Each alloy sample was superheated for some time at a temperature well above the liquidus, after which the thermocouples were placed in position. The rate of cooling employed was about 1.3° per minute. The thermal-arrest temperatures were taken from the alloy-temperature data, and the differential temperature readings provided a sensitive check on the position of these arrests. The alloys were analyzed for iron after the experiments were completed. The results, together with a few results obtained by the same method at the lower peritectic temperature on alloys made from the same lot of zinc, are given in Table 5. The peritectic data will be discussed later.

The freezing temperature of these alloys was consistently $419.40 \pm 0.05^{\circ}$ when compared to the sample of pure zinc certified to have a freezing point of 419.45° . Hence, on the basis of thermal analysis alone, it must be concluded that, if a eutectic exists, the lowering of the freezing point of zinc is not more than 0.05° . This question will be discussed later in connection with the work on the solid solubility of iron in zinc.

Peritectic Arrests

The upper peritectic horizontal of the iron-zinc equilibrium diagram indicates the temperature at which a reversible reaction occurs between

a solid solution of zinc in gamma iron, the melt (zinc saturated with iron), and a solid phase designated as $\text{Fe}_3\text{Zn}_{10}$ ⁷. Similarly, the lower peritectic horizontal corresponds to the temperature at which a reversible reaction occurs between the liquid, the solid phase designated as $\text{Fe}_3\text{Zn}_{10}$, and the solid phase lower in iron, designated as FeZn_7 .

TABLE 5.—*Thermal Data on Alloys Containing Small Amounts of Iron*

Alloy No.	Fe		Zinc, Per Cent	Thermal Arrests, Deg. C.
	Per Cent Synthetic	Per Cent Final Analysis		
A5686	0.0009	0.001	Remainder	419.40 ± 0.05
A5398	0.016	0.017	Remainder	419.40 ± 0.05
A5588	0.10	0.09	Remainder	419.40 ± 0.05
A5590	1.0	1.0	Remainder	419.40 ± 0.05
A5674	2.5	2.6	Remainder	657.8 ± 0.2
A5649	2.75	2.8	Remainder	658.0 ± 0.2
A5648	3.0		Remainder	658.0 ± 0.2

According to the older data on the iron-zinc system, the upper peritectic temperature was placed at about 773°, and the solubility of iron in zinc at this temperature was about 11 per cent. Thus, if evidence of the occurrence of the peritectic reaction could be obtained in an alloy containing substantially less than 11 per cent Fe, that would constitute independent evidence that the earlier solubility curve was incorrect. Such evidence has been obtained in the present work. The lower peritectic horizontal was previously located at about 658°, terminating in the former liquidus at about 3.6 per cent Fe.

In the first cooling-curve experiments tried (Table 5), thermal arrests were obtained at about the previously accepted temperature of 658°. There was in each instance a slight undercooling followed by a sudden evolution of heat, which was sufficient to produce a slight rise in temperature but was not sufficiently prolonged to produce a truly horizontal portion on the cooling curve.

Cooling curves were then obtained on three flux-covered alloys containing from 8.5 to 11 per cent Fe, at both peritectic temperatures. The results in each experiment were similar to the preceding, except that as the iron content of the samples increased, so also did the maximum temperature attained during the thermal arrest without, however, resulting in the production of a constant maximum temperature.

It was then decided to run both heating and cooling curves in the remaining experiments. At the same time certain other changes were made. The heating and cooling rate was lowered to 0.4° to 0.5° per

⁷ Use is made of the formulas FeZn_7 , $\text{Fe}_3\text{Zn}_{10}$, etc., in this paper as a matter of convenience, but it is not intended thereby to indicate the correctness of these formulas.

minute. In order to check the reproducibility of the results, several consecutive runs were made on the same alloy. Because of the tendency of the zinc to oxidize at the higher temperatures, the use of a flux-covered melt in an open crucible was abandoned, and the alloys were sealed, under a partial atmosphere of hydrogen, in a silica-tube crucible provided with a re-entrant protection tube for the thermocouple. The pressure of hydrogen was adjusted so that, at the highest temperature to be used, the total pressure in the sealed crucible would be about one atmosphere.

The alloys were either specially prepared by dissolving the required amount of iron in zinc, or were prepared from the alloys remaining from the high-temperature solubility experiments⁸. The brittle materials were ground to pass 48 mesh and were carefully mixed, sampled and analyzed for iron. About 175 to 200 grams of each alloy was placed in a crucible, the thermocouple tube was inserted and the top of the tube sealed on. The crucible was then evacuated and partly filled with hydrogen through a small side tube, after which the latter was sealed off.

A series of heating and cooling curves was then obtained, in the order shown in Table 6, for alloys No. 100, No. 107-A and No. 111. The melt was maintained at a temperature a few degrees above or below the particular peritectic temperature to be examined for from 3 to 18 hr. before each run. The calibrated couples were in place only during a run and were checked before and after a series, each of which required about four days to complete. Upon finally cooling a few degrees below the lower peritectic temperature, the crucible always split open, probably because of the expansion caused by the peculiar production of voids when FeZn_7 is formed.

The results obtained are contained in Table 6, and Figs. 2 and 3 show typical heating and cooling curves obtained on alloys containing 11.1 and 20.0 per cent Fe, respectively.

From a study of these results, it is concluded that within the experimental error, the peritectic temperatures must lie, respectively, between 661° and 672° , and between 781° and 782° . Because of the prolonged constant temperature arrests obtained with heating curves, it is concluded that the best values are $672 \pm 1^\circ$ and $782 \pm 1^\circ$, respectively, corresponding to heating-curve arrests on alloys containing approximately the maximum amounts of the two reacting phases, respectively FeZn_7 (10.9 per cent Fe) and $\text{Fe}_3\text{Zn}_{10}$ (20.4 per cent Fe).

It is obvious from the data of Table 6 that thermal arrests were obtained at the upper peritectic with alloys containing less than 11 per

⁸ Alloy No. 100, containing 20.0 per cent Fe, was prepared from an equally pure iron-zinc alloy made several years ago by one of the authors (J. L. R.) by heating the metals in a bomb under 5 atmospheres pressure of nitrogen for 48 hr. at 1100° , and slowly cooling.

cent Fe, and that therefore the old liquidus curve must have been incorrectly located. The fact that the new liquidus curve fits in well with the new peritectic temperatures may be considered as mutual confirmation by each of the correctness of the others.

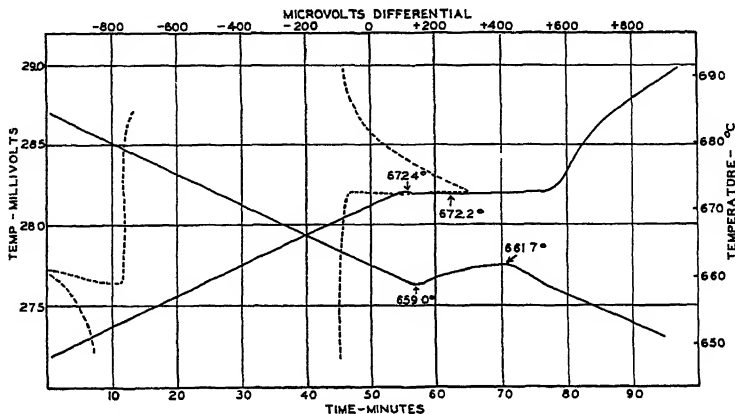


FIG. 2.—THERMAL ARRESTS AT LOWER PERITECTIC. COOLING CURVE, TEST NO. 6, AND HEATING CURVE, TEST NO. 1, FOR ALLOY NO. 107A, CONTAINING 11.1 PER CENT FE.

Solid lines are time-temperature curves and broken lines are differential-temperature curves.

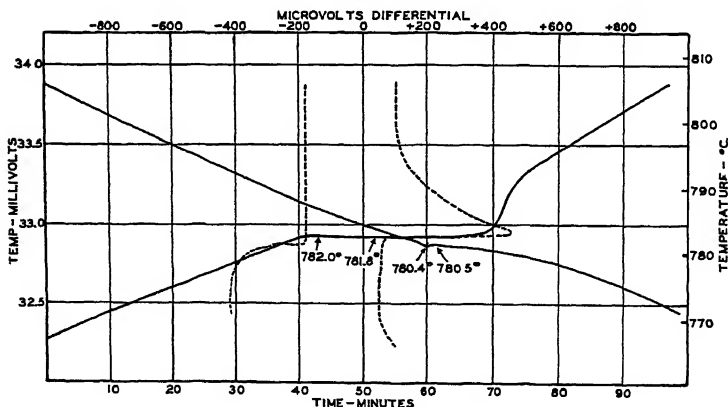


FIG. 3.—THERMAL ARRESTS AT UPPER PERITECTIC. COOLING CURVE, TEST NO. 3, AND HEATING CURVE, TEST NO. 2, FOR ALLOY NO. 100, CONTAINING 20.0 PER CENT FE.

Solid lines are time-temperature curves and broken lines are differential-temperature curves.

On several occasions the heating and cooling curves were extended to include the region crossed by the liquidus, but no results of value were obtained. Once or twice a very slight and gradual change of slope was observed, but no definite temperature could be assigned to this

change. This condition existed in experiments at temperatures from the lower peritectic up to about 875°.

SOLID SOLUBILITY MEASUREMENTS

It was desired to use as many experimental methods as possible in fixing the solid solubility of iron in zinc, since previous experience⁹ has

TABLE 6.—*Location of Peritectic Temperatures from Thermal Data*

Alloy No.	Fe, Per Cent		First Thermal Arrest				Second Thermal Arrest			
			Temperature, Deg. C.		Duration of Constant Temp., Min.	Type of Curve	Temperature, Deg. C.		Duration of Constant Temp., Min.	Type of Curve
	Initial	Final	Maximum	Minimum			Maximum	Minimum		
96-7 ^a	8.6	9.3	770.1	769.5	None	Cooling	660.0	658.1	None	Cooling
98-2 ^a	9.4	11.4	773.4	771.6	None	Cooling	660.8	657.8	0.5	Cooling
96-8	8.6		774.8 ± 0.1		None	Cooling	661.3	658.7	2.0	Cooling
100	20.0						None observed			Heating
100	20.0		782.0	781.8	10	Heating				
100	20.0		780.5	780.4	1	Cooling				
100	20.0		781.8	781.6	10	Heating				
100	20.0		780.4		None	Cooling				
100	20.0						None observed			Cooling
107-A	11.0	11.1					672.4	672.2	15	Heating
107-A	11.0	11.1	782.6		2	Heating				
107-A	11.0	11.1	777.0 ± 0.1		None	Cooling				
107-A	11.0	11.1	781.7	781.4	2	Heating				
107-A	11.0	11.1	777.3		2	Cooling				
107-A	11.0	11.1					661.7	659.0	None	Cooling
111 ^b	8.5	8.3					673.9	673.0	10	Heating
111 ^b	8.5	8.3	783.9 ± 0.1		None	Heating				
111	8.5	8.3	None observed			Cooling				
111	8.5	8.3	782.7 ± 0.1		None	Heating				
111	8.5	8.3	776.4 ± 0.1		None	Cooling				
111	8.5	8.3					660.7	658.5	2	Cooling

^a Cooling rate about 1.2° per minute; all other rates were 0.4°–0.5° per minute.

^b At the end of the second run on this alloy it was noted that the thermocouple junction was about one inch above its normal position of $\frac{3}{4}$ in. from the bottom of the crucible. It is believed that this condition also existed during the first run, thus accounting for the high temperatures obtained on these two heating-curve arrests.

shown that a single method frequently cannot give a reliable answer in such solubility measurements. Microscopical and X-ray examination, conductivity measurements and magnetic-susceptibility determinations all were used in the present work, but only the microscope gave useful results. The microscopical experiments will be described in detail, after which a brief summary of the results obtained by the other experimental methods will be given.

⁹ E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: *Trans. A.I.M.E.*, (1934) **111**, 264.

Microscopical Examination

The alloys used in this part of the work were prepared from Armco iron and the special lot of zinc of which the analysis is given on page 201. With this very pure zinc, there was no difficulty due to the presence of tiny particles, at the grain boundaries of the microsections, which might be mistaken (in this case) for iron-zinc compound particles. This is an important point, for even a few thousandths of a per cent of lead may furnish enough particles at the dendrite boundaries of a zinc microsection to be mistaken for the appearance of a new phase, especially when, as with iron, the solubility limit is extremely low. It is possible that in the past, with the less pure zinc used, iron particles actually were present but were mistaken for particles of lead.

The compositions of the alloys used in all of the solid solubility work are given in Table 7. These alloys were prepared by the direct addition

TABLE 7.—*Composition of Alloys Used in Solid Solubility Experiments*

Alloy No.	Fe	
	Per Cent Synthetic	Per Cent Analyzed
A5386		0.0009
A5517	0.002	0.0028
A5592	0.004	0.004
A5593	0.006	0.006
A5594	0.008	0.008
A5595	0.010	0.010
A5596	0.012	0.012
A5597	0.014	0.014
A5598	0.016	0.017

of the iron and cast from a temperature of 500° to 550° into iron molds at 150°, in the form of 6 by 3 by $\frac{5}{8}$ -in. slabs and as 6 by $\frac{7}{8}$ -in. rods. The slabs were homogenized at 375° for 10 days, hot-rolled to 0.040-in. thickness and then cold-rolled in easy passes to a final gage of 0.020 in. Specimens for conductivity measurements, microscopical examination and chemical analysis were cut from the cold-rolled alloy in such a manner as to provide a representative sampling of the entire coil. Cast specimens for microscopical examination were taken from the 6 by $\frac{7}{8}$ -in. rods.

The alloys listed in Table 7 were examined in both the cast and rolled form after annealing at 150° and 400°, respectively, and in the cast form after annealing at 375°. It was not thought necessary to reproduce all of the photomicrographs, but the annealing treatments indicated with the photomicrographs shown in Figs. 4, 5 and 8 were used with all of the alloys in the series.

All cast specimens except those finally annealed at 400° received a preliminary homogenizing treatment of 10 days at 375° followed by air-cooling. The rolled specimens received a preliminary flash-annealing in oil at 275° for 2 min., followed by an annealing of 11 weeks at 150°, except that the specimens finally annealed at 400° received no flash-annealing. The alloy containing 0.0028 per cent Fe was added to the series near the end of the work and was examined only in the cast condition.

The microsections were prepared essentially as described in an earlier paper¹⁰. The etching reagent contained 200 grams of CrO₃ and 15 grams of Na₂SO₄ per liter of water. Specimens photographed at a magnification of 1000 were etched about one second, those photographed at 100 magnification for a somewhat longer time. Specimens were prepared and photomicrographs taken within 48 hr. of the final quenching.

Placing of the solid solubility boundary was based on careful examination of the microspecimens under an oil-immersion objective at high magnification. Structures observed at low magnification confirmed the conclusions drawn. Observations at 150° and 400° showed the solid solubility limit to be between 0.0009 and 0.0028 per cent Fe. Since even after annealing at 400° the FeZn₇ particles have a tendency to line up along what may be regarded as dendrite boundaries, even when the concentration falls as low as 0.004 per cent Fe, it is believed that the solubility is also substantially unchanged from 400° right up to the melting point. The conclusion is based on the assumption that submicroscopic particles in the dendrite boundaries of the cast alloys usually act as points of concentration (i.e., grow) during subsequent annealing. The photomicrographs shown in Figs. 4, 5 and 8 plainly show the solubility limits.

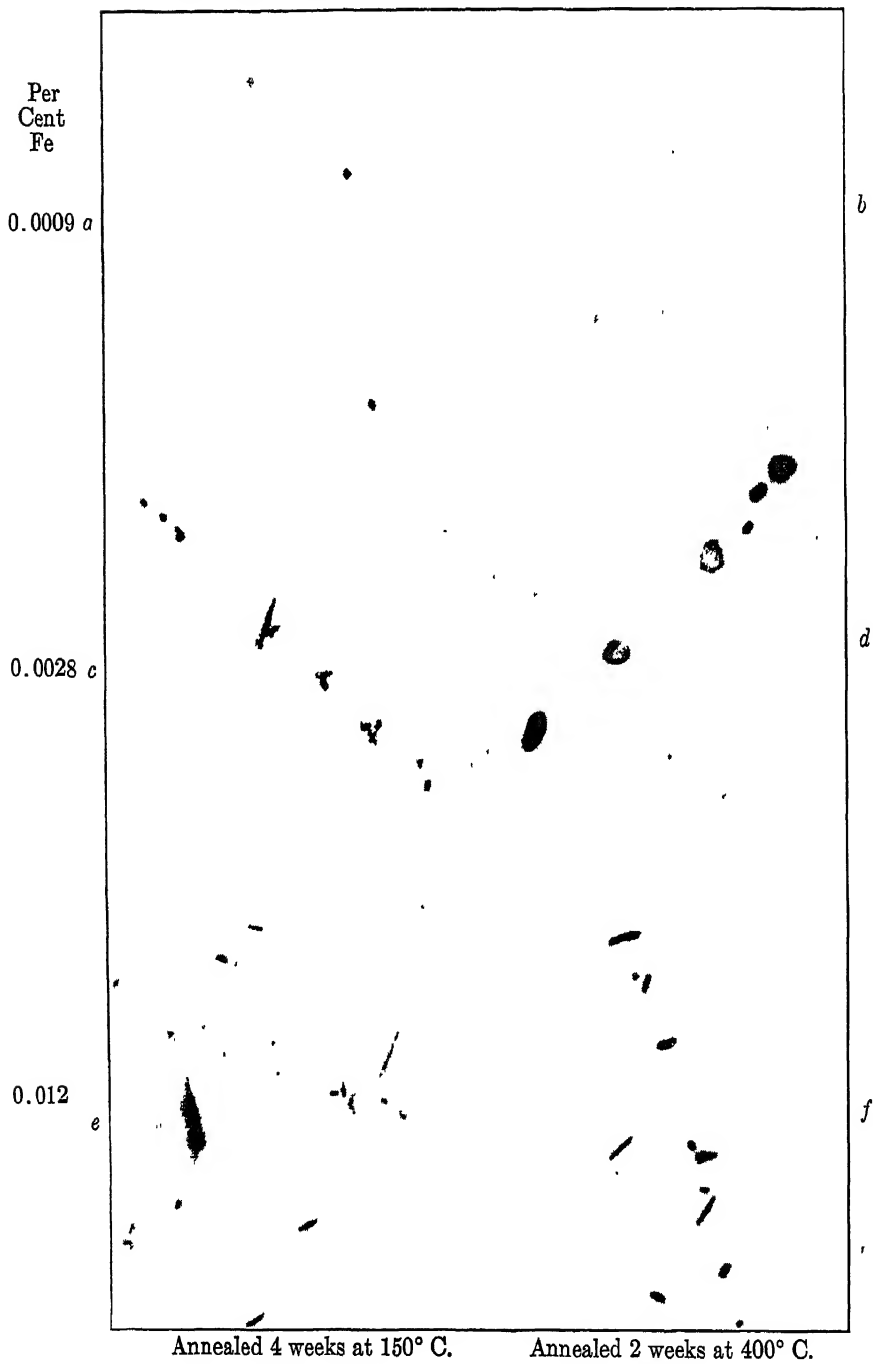
Electrical Conductivity

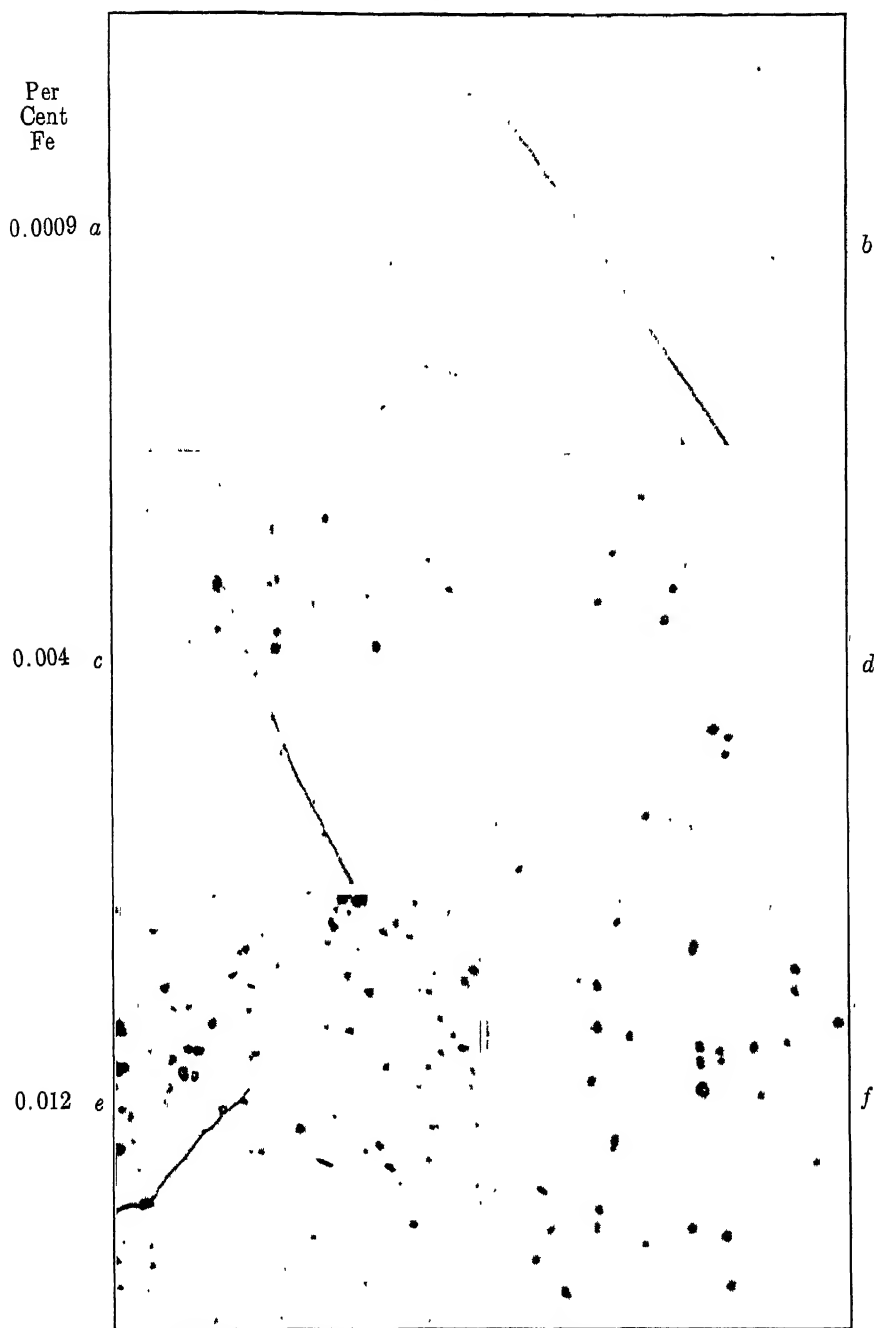
For this work strips were cut from the cold-rolled alloy coils and flash-annealed for 2 min. in oil at 275° in a special tube. The strips were then heated for 11 weeks at 150° in a furnace having a carefully controlled uniform temperature zone, and quenched. No further annealing treatments were carried out in view of the peculiar results obtained on this first annealing treatment. The experimental technique employed was the same as that described in an earlier paper¹¹. The results obtained with the entire series of alloys, with the exception of alloy No. A5517, which was available only in the cast form, corresponding to the equilibrium condition existing after 11 weeks annealing at 150°, are shown in Fig. 6.

On the basis of conductivity data alone, it might have been concluded that the solid solubility limit should be placed at about 0.006 per cent Fe, but because this value was so much higher than that obtained by

¹⁰ J. L. Rodda: Preparation of Graded Abrasives for Metallographic Polishing. *Trans. A.I.M.E.* (1932) **99**, 149-158.

¹¹ E. A. Anderson et al.: Reference of footnote 9.

FIG. 4.—CAST, ANNEALED IRON-ZINC ALLOYS. $\times 1000$.



Annealed 11 weeks at 150° C. Annealed 2 weeks at 400° C.
FIG. 5.—ROLLED, ANNEALED IRON-ZINC ALLOYS. $\times 1000$.

microscopical examination, it was decided to attempt to locate the solid solubility limit by means of X-ray analysis. The latter partly explains the peculiar shape of the conductivity curve.

X-ray Measurements

Specimens for the X-ray analysis were cut from the conductivity strips of which the annealing treatment has been described, for the alloys ranging from straight zinc up to 0.010 per cent Fe.

The X-ray examination disclosed the fact that no detectable difference could be found between the lattice dimensions of pure zinc and those of the alloy containing 0.010 per cent Fe. These measurements, which were very carefully made, are at variance with the results reported by Stillwell and Clark¹², who claimed to have detected a change in the axial ratio



FIG. 6.—VARIATION OF ELECTRICAL CONDUCTIVITY WITH IRON CONTENT IN QUENCHED SPECIMENS PREVIOUSLY IN EQUILIBRIUM AT 150° C.

of zinc to 1.885 (from the accepted value of 1.865), produced by solid solution of iron in zinc during the formation of a galvanized coating. It is difficult to believe that as little as 0.0028 per cent Fe could produce such a considerable change in the axial ratio; no such change was observed in our own experiments, which included an 0.010 per cent Fe alloy, in which the iron was far in excess of the solubility limit.

The X-ray patterns obtained from this series of alloys did, however, show differences in the crystal orientations of the several alloys that roughly paralleled the conductivity values. While there is undoubtedly a close relation between the X-ray and conductivity data, it is not felt that orientation alone can be responsible for the shape of the conductivity curve. For, while conductivity measurements involve the entire cross-section of the strip, the X-ray results are obtained from a surface layer only, and differences in grain size produced by a variation in the amount of iron present must be considered.

¹² C. W. Stillwell and G. L. Clark: *Jnl. Ind. & Eng. Chem., Anal. Ed.* (1930) **2**, 266-72

It is concluded, therefore, that the break in the conductivity curve at 0.006 per cent Fe does not indicate the solid solubility limit of iron in zinc.

Measurements of Magnetic Susceptibility

The magnetic susceptibility of an alloy containing 1.1 per cent Fe was measured. The alloy was paramagnetic with a susceptibility of $+1.99 \times 10^{-7}$. Pure zinc is diamagnetic with a value of -1.1×10^{-6} . Since the change in susceptibility produced by 1.1 per cent Fe is so slight, it is evident that the effect of a few thousandths of a per cent of iron would be negligible. Such measurements cannot, therefore, be used to determine the solid solubility of iron in zinc.

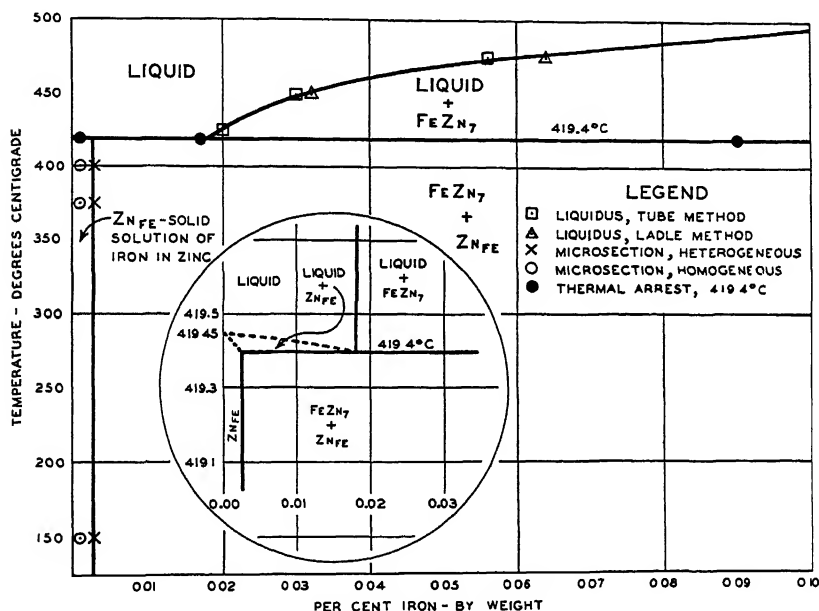


FIG. 7.—EUTECTIC REGION AND SOLID SOLUBILITY BOUNDARY IN IRON-ZINC SYSTEM.

A large-scale equilibrium diagram of the region around the melting point of pure zinc is shown in Fig. 7. This is based upon the value of 419.45 for the freezing point of a sample of pure zinc¹³, a value of 419.40 for the melting point of zinc containing 0.0009 per cent or more of iron, the maximum of 0.0028 per cent Fe for the limit of solid solubility, and an extrapolation of the liquidus curve obtained by direct sampling of molten alloys down to 425°. It thus appears that, within the experimental error, the eutectic lowering of the freezing point of zinc is not more than 0.05°, and the eutectic composition contains not more than 0.018 per cent Fe.

¹³ The value of 419.45°, reported in an earlier paper by W. F. Roeser and H. T. Wensel [*Jnl. U.S. Bur. Stds.* (1933) 10, 275] is altered in a more recent paper [*Ibid.* (1935) 14, 255], without further discussion, to read 419.48° C.

DISCUSSION OF RESULTS

In the following discussion emphasis is placed upon the various ways in which the experimental technique differed from that used by earlier investigators.

Direct sampling of the melt in the presence of excess iron at a series of temperatures, and by several methods, has not previously been employed. The results indicate that considerable confidence may be placed in the conclusion that these solubility data were obtained under truly equilibrium conditions. The fact that the difference between our results and the earlier ones becomes greater with increasing temperature is a strong indication that the synthetic alloys frequently used by earlier workers were less completely saturated with iron at the higher temperatures and therefore gave increasingly greater apparent solubility values.

The observance of a well defined thermal arrest, corresponding to a point on the upper peritectic, with several alloys containing less iron than that required by the former solubility curve, is definite proof that the latter curve was incorrectly located at and near the peritectic temperature. The regularity of the present liquidus and peritectic data strengthens the conclusion that the former liquidus curve was incorrectly located at all temperatures.

Our failure to observe thermal arrests corresponding to the liquidus is the most serious difference between the new work and the old. The liquidus curve in this system is relatively steep, so that no large evolution of heat should be expected. In the present thermal experiments the thermocouple junction was purposely located near the bottom of the crucible to detect a reaction between solid phases that would be concentrated there, and it may be that a position nearer the middle of the melt would have been better for the detection of a weak primary arrest. On the other hand, it is certain that the present thermal analyses were carried out by a much more sensitive apparatus, and at a much slower cooling or heating rate, than were the earlier experiments.

The fact that heating curves are better than cooling curves for the accurate location of peritectic reaction temperatures is not new, but it is the first time that such heating curves have been used with iron-zinc alloys.

In exploring an alloy system, it is customary to locate vertical phase boundaries by means of the alloy composition giving the most prolonged thermal arrest. This method was not employed in the present investigation, however, because the compositions of the two phases involved, FeZn_7 and $\text{Fe}_3\text{Zn}_{10}$, have already been determined more accurately by X-ray analysis than could be done by the thermal method.

It has been necessary to place the entire responsibility for the determination of solid solubility upon the microscope, which has the advantage

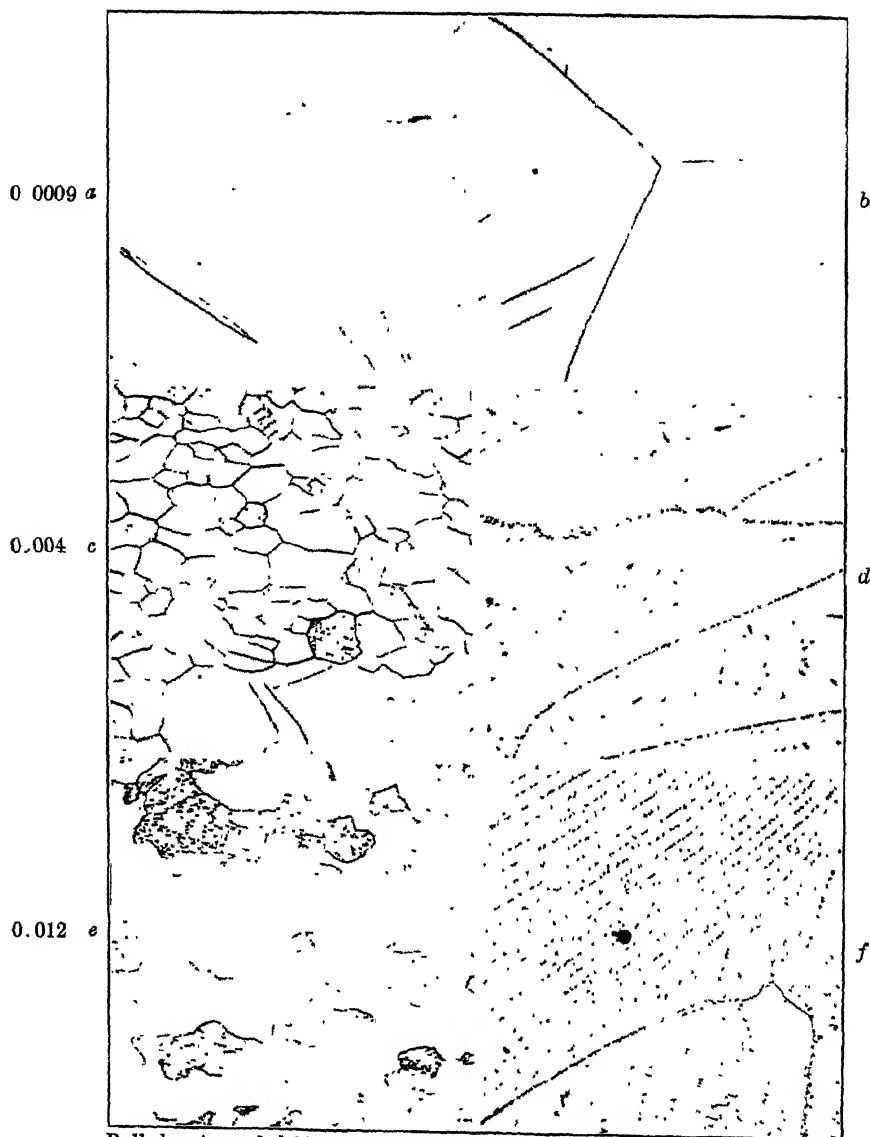
of being able to detect directly the first appearance of a new phase. For reasons already given, electrical conductivity, X-ray, and magnetic-susceptibility measurements were unsuited for the determination of the solid solubility limit.

The new low solid solubility limit of iron in zinc will have an important effect on the interpretation of the microstructure of zinc. Until very recently, very little zinc containing less than 0.0028 per cent Fe has been available and it is obvious that, unless iron is kept well below this limit in alloys of zinc with other elements, there is danger of mistaking the FeZn_7 particles for the secondary phase of the system being investigated. Even when the size of the FeZn_7 particles is below the resolving power of the microscope, they seem to produce etching pits visible even at low magnification. Such etching pits are visible on some of the photomicrographs included in this paper, but not on the photomicrographs of the alloy containing only 0.0009 per cent Fe.

The available evidence, while not complete, is all in favor of the existence of a eutectic transformation about 0.05° below the melting point of pure zinc. The solid solubility of iron in zinc is so low that a eutectic lowering of only 0.05° is not impossible. The iron-zinc diagram cannot be complete without some transformation at this temperature, and the alternative, the existence of a peritectic transformation, seems very unlikely. There is no microscopical evidence that a new phase (for example, the FeZn_{10} phase claimed by some investigators) other than FeZn_7 is produced; on the other hand, the appearance of the 100X micro-sections in Fig. 8 is strong evidence that a eutectic reaction is involved in the formation of the iron-zinc crystals. If a peritectic reaction did occur, it would in all probability be at a higher, rather than a lower temperature than the melting point of pure zinc. The existence of another peritectic horizontal has never been detected by thermal analysis, and the smooth liquidus curve established by the present work is strong evidence that a third break in that curve similar to those produced by the 672° and 782° peritectic horizontals does not exist.

ACKNOWLEDGMENTS

The authors wish to take this means of acknowledging the assistance of many other members of the Research Division of The New Jersey Zinc Co., whose help in these experiments was greatly appreciated, but especially the following: Messrs. E. A. Anderson and R. K. Waring, under whose direction this work was done, for their helpful advice and criticism; Mr. C. F. Homewood, who designed and constructed the thermal analysis apparatus, and who made the magnetic susceptibility measurements; Mr. J. R. Bossard, who carried out the thermal analyses; and Mr. M. L. Fuller, who made the X-ray measurements.



Rolled. Annealed 11 weeks at 150° C. Cast. Annealed 4 weeks at 375° C.
 FIG. 8.—ANNEALED IRON-ZINC ALLOYS. $\times 100$.

PART II.—PRESENT STATUS OF THE IRON-ZINC EQUILIBRIUM DIAGRAM

Because there has been a considerable gap between the early work on the iron-zinc system, which was done from 25 to 30 years ago, and the few papers that have appeared in recent years utilizing modern experimental methods, it seemed desirable to attempt to correlate all of the available data and to bring our knowledge of the system up to date¹⁴.

A large-scale diagram was prepared on which were plotted points corresponding to all of the data in the literature. After a critical study of the original papers, and with the plotted points as a guide, solid lines were drawn on the diagram in what seemed to be their most probable location. In addition, broken lines were added to complete the boundaries of certain phases of which the exact limits were doubtful, but for which it seemed that provision should be made. This diagram, with the experimental points deleted, is shown in Fig. 9, and serves as the basis of the following discussion.

LIQUIDUS CURVE AND RELATED AREAS

The original work on this system was done in 1906 by von Vegesack¹⁵, a student of G. Tammann, and his data have been incorporated in all of the diagrams of the system published up to the present. A study of his description of the experiments shows that, when compared with the present authors' experiences in preparing iron-zinc alloys, von Vegesack's alloys were not properly prepared at the higher temperatures, and that many of them undoubtedly contained free iron, which he assumed to be all in solution. In fact, this same criticism may properly be made of most of the alloys prepared by all of the earlier workers and by some of the later ones. As a result, the liquidus curve established by von Vegesack by means of cooling-curve arrests corresponded to a larger amount of iron at a given temperature than actually was in solution, and the curve lay too far to the right on the diagram. Moreover, the peritectic arrests reported by him were undoubtedly obtained, in some cases at least, with alloys that were not saturated with iron because sufficient time had not been allowed for solution to occur; thus the observed peritectic temperatures may have been too low. Finally, the accuracy of von Vegesack's temperature measurements and his technique in obtaining cooling curves leaves much to be desired.

Von Vegesack placed the melting point of zinc at 419°, the lower peritectic horizontal at 662° and the upper one at 777°. He established the formulas of the phases formed by the peritectic reactions by means of the alloy composition giving the most prolonged thermal arrest, and he

¹⁴ While this manuscript was in proof, a review of some of the literature bearing on the iron-zinc equilibrium diagram, by W. D. Jones and R. T. Parker, appeared in *The Metallurgist*, supplement to *The Engineer* (Aug. 30, 1935) 56-58.

¹⁵ A. von Vegesack: *Ztsch. anorg. Chem.* (1906) **52**, 30-40.

gave these as FeZn_7 and FeZn_3 . He also claimed to have observed another peritectic reaction at 422° , but later this was disproved by several workers, and undoubtedly was merely an error in determining the eutectic arrest at 419° . The solubility of iron in zinc was given by him as 0.7 per cent at the melting point of zinc, rising to about 12 per cent at 817° .

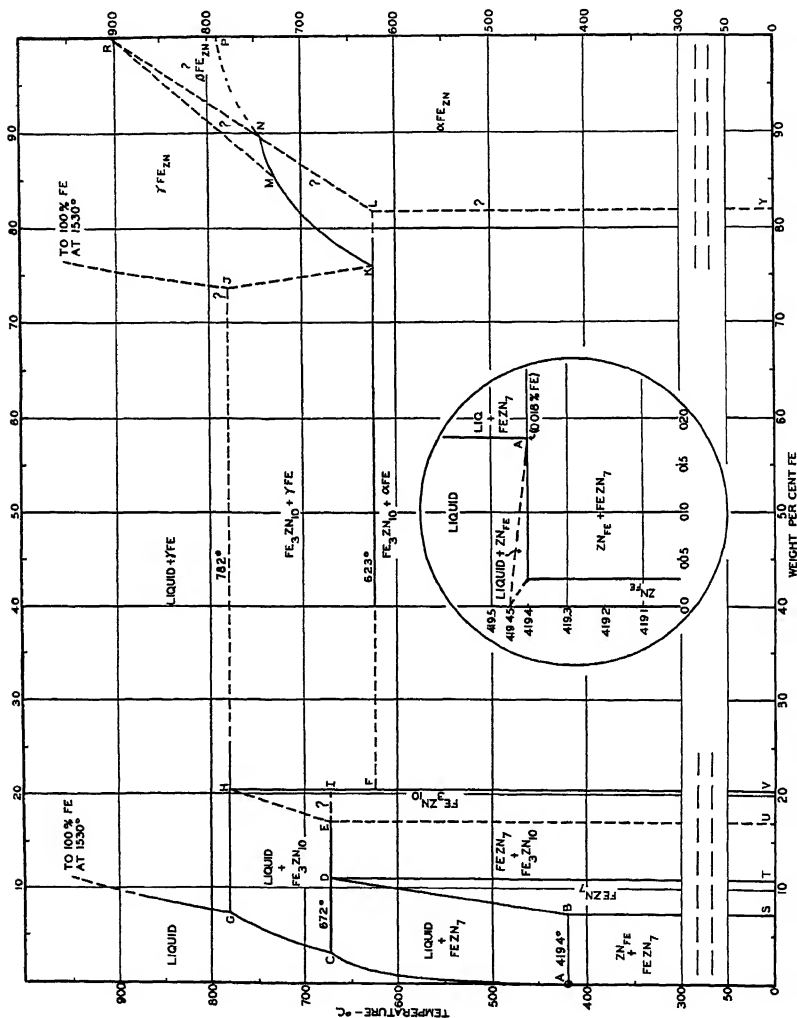


FIG. 9.—EQUILIBRIUM DIAGRAM OF IRON-ZINC SYSTEM ACCORDING TO BEST INTERPRETATION OF ALL AVAILABLE DATA.

Broken lines (except line PN) represent phase boundaries not yet experimentally located.

Wologdine¹⁶, a student of Le Chatelier, investigated a part of the iron-zinc system in 1907. He prepared and ran cooling curves on 16 alloys containing up to 9.5 per cent of iron. His data on the liquidus curve and on the eutectic temperatures seem to be almost entirely worthless even when compared to that of von Vegesack. He did, however, find micro-

¹⁶ S. Wologdine: *Rev. de Mét.* (1907) 3. 539-546.

scopic evidence of excess iron at room temperature in alloys containing more than 0.07 per cent Fe, thus considerably lowering the solubility limit set by von Vegesack. Wologdine seems to have devoted most of his efforts to proving the existence of FeZn_{10} by means of chemical isolation and analysis of the iron-zinc crystals formed in his alloys, but his evidence is not convincing. Several years later Le Chatelier¹⁷, engaging in a polemic with Taboury¹⁸, said that "Wologdine . . . established thermally, chemically and microscopically the existence of FeZn_{10} " Wologdine actually did none of these things, but it is interesting that the existence of FeZn_{10} has recently been claimed anew on the basis of some incomplete X-ray data, which will be referred to later.

In 1910 Arnemann¹⁹ in effect repeated much of von Vegesack's work, making use of some of the improvements in experimental technique which had been developed in Tammann's laboratory. The experimental results agreed essentially with those of von Vegesack, but apparently were not reliable above 10 per cent of iron. As with the previous work, the preparation of the alloys, according to present criteria, was unsatisfactory. Arnemann set the solid solubility of iron in zinc as low as 0.06 per cent, and pointed out the impossibility of having a peritectic reaction at 422° between the liquid and FeZn_7 to form a phase containing 0.7 per cent Fe, as postulated by von Vegesack. Arnemann gave the composition of the material from 0.06 to 7.3 per cent Fe as a mixed phase composed of the solid solution and FeZn_7 ; from 7.3 to 10.9 per cent Fe, homogeneous FeZn_7 , which showed a range of composition because of the solubility of Zn in FeZn_7 ; from 10.9 to 22.2 per cent Fe, FeZn_7 plus FeZn_3 . The peritectic horizontals, obtained by cooling curves, were given by Arnemann as 667° and 780° , respectively.

Arnemmann was unable to detect any evidence of an alpha-beta zinc transformation as proposed by Le Chatelier²⁰ in 1890. This question of the allotropy of zinc has been disposed of in recent years by X-ray studies²¹ from which it may be concluded that not more than one crystal modification of zinc exists.

¹⁷ H. Le Chatelier: *Compt. rend.* (1914) **159**, 356-57.

¹⁸ F. Taboury: *Ibid.* (1914) **159**, 241-43.

¹⁹ P. T. Arnemann: *Metallurgie* (1910) **7**, 201-11.

²⁰ H. Le Chatelier: *Compt. rend.* (1890) **111**, 454.

²¹ W. M. Peirce, E. A. Anderson and P. Van Dyck: *Jnl. Frank. Inst.* (1925) **200**, 349-61.

P. Sillers: U.S. Bur. Stds. *Sci. Pub.* (1926) **20**, 686-95.

Apparently unaware of the two preceding papers, three additional papers have appeared claiming the detection of allotropic changes in zinc by microscopic and electrochemical methods:

D. Stockdale: *Jnl. Chem. Soc.* (1925) **127**, 2951.

G. I. Petrenko: *Ztsch. anorg. Chem.* (1927) **162**, 251; (1927) **167**, 411.

Peirce²², summarizing work that had been done in the Research Division of the New Jersey Zinc Co., gave the solid solubility of iron in zinc as about 0.02 per cent at the melting point of zinc and indicated a possible eutectic at about 0.04 per cent Fe. Later Peirce and Marshall²³ reported the solid solubility as being about 0.008 per cent Fe, and again reported the possible existence of a eutectic. Cooling-curve arrests indicated the peritectic temperatures to be 658° and 773°, respectively, and the eutectic temperature to be 418°.

Ogawa and Murakami²⁴, in 1928, prepared two series of iron-zinc alloys, one containing up to 30 per cent Fe, the other from 30 to 90 per cent Fe. Most of the alloys were prepared by grinding a brittle mother alloy containing 8 to 10 per cent Fe to a fine powder and mixing with the required amount of pure iron powder. Work with the alloy series high in iron will be discussed later; the first series of alloys was used to obtain cooling curves by packing the mixtures into tubes and heating "under hydrogen atmosphere to 680° for 3 hr., and after raising to 800° slowly cooling." Even though the powdered metals were used, it seems very doubtful that any of the alloys above about 8 per cent Fe could have been made homogeneous, or that saturation of the liquid with iron had occurred. The observed peritectic temperatures of 647° and 766°, respectively, are so much lower than any others reported as to indicate that the authors' cooling curves were not satisfactory. The melting point of zinc was placed at 419°.

Grubitsch²⁵ attempted to determine both the solubility and rate of solution of Armco iron in C.P. zinc as a function of temperature, but reported no equilibrium solubility results.

As a result of the work reported in Part I of the present paper, the authors have shown by direct sampling of a series of melts in thermal equilibrium that the solubility of iron in molten zinc is lower at all temperatures than had previously been supposed. Heating curves have been shown to be more reliable than cooling curves as a means of detecting peritectic reaction temperatures and the new values of 672° and 782°, respectively, have been obtained. The eutectic region has been examined and a new low value for the solid solubility of iron in zinc obtained. The corresponding lines on the diagram of Fig. 9 were drawn to fit all of these new results.

IRON-ZINC ALLOY PHASES

Since most of the papers that remain to be discussed deal with several of the various phases, further subdivision of this review would be imprac-

²² W. M. Peirce: *Trans. A.I.M.E.* (1923) **68**, 771.

²³ L. H. Marshall and W. M. Peirce: *Amer. Soc. Steel Treat. Handbook* (July, 1928) 1233.

²⁴ Y. Ogawa and T. Murakami: *Tech. Repts. Tohoku Imp. Univ.* (1928) **8**, 53-69.

²⁵ H. Grubitsch: *Stahl und Eisen* (1931) **51**, 1113-1116.

tical except as to experimental methods and, in general, the remaining material will be discussed in more or less chronological order. To facilitate the discussion, Table 8 has been prepared to indicate the composition of the various alloy phases that are formed, or which have been claimed to exist, in the iron-zinc system.

TABLE 8.—*Composition of Various Hypothetical Alloy Phases*

Atomic Ratio	Fe		Zn, Weight Per Cent	Remarks
	Atomic Per Cent	Weight Per Cent		
FeZn ₁₀	9.09	7.87	92.13	Claimed microscopically and by X-ray in galvanized coatings. Not proved. Body-centered cubic structure?
FeZn ₇	12.5	10.88	89.12	Found by all investigators. Close-packed hexagonal. Apparently dissolves zinc in solid solution.
Fe ₃ Zn ₂₁	19.1	16.90	83.10	Claimed as an equivalent structure to Fe ₃ Zn ₁₀ on theoretical grounds from X-ray data. Body-centered cubic structure.
Fe ₃ Zn ₁₀	23.07	20.40	79.60	Established by most of the X-ray data as being the correct formula of the material originally called FeZn ₃ . Body-centered cubic.
FeZn ₃	25.0	22.16	77.84	See Fe ₃ Zn ₁₀ .
FeZn.....	50.0	46.07	53.93	No evidence.
Fe ₃ Zn ₂	60.0	56.17	43.83	No evidence.
Fe ₃ Zn.....	75.0	71.93	28.07	Doubtful; e.m.f. data only.
Fe ₅ Zn.....	83.3	81.03	18.97	Doubtful; e.m.f. data only. May possibly be the approximate composition of the solid solution of Zn in Fe.
Fe ₇ Zn.....	87.5	85.67	14.33	No evidence.

Electrode Potential Measurements

Vigouroux, Ducelliez and Bourbon²⁶ prepared iron-zinc alloys by fusing together fine iron powder and excess zinc in a current of hydrogen at about 1000°. Distillation of the zinc proceeded until it was judged that approximately the desired alloy had been formed. Electrode potential measurements were then made with pieces of these alloys against a pure zinc electrode in 0.05 N. zinc sulfate solution. Upon plotting the observed potential against the (presumably analyzed) alloy composition,

²⁶ E. Vigouroux, F. Ducelliez and A. Bourbon: *Bull. Soc. Chim. France* (1912) 11, 480-485.

breaks were found in the curve which were believed to correspond to the presence of FeZn_7 , FeZn_3 , Fe_3Zn and Fe_5Zn .

Taboury²⁷, after establishing by chemical separation and analysis of iron-zinc crystals from a galvanizing bath, which had been kept just above the melting point of zinc for months, that von Vegesack's assumption of a separate phase containing 0.7 per cent Fe was incorrect, found these crystals to contain 7.1 to 7.3 per cent Fe, and probably correctly assumed them to be FeZn_7 "wet with zinc." He did not mention the possible existence of FeZn_{10} , and this omission drew a sharp retort from Le Chatelier²⁸. Taboury also claimed to have repeated some of the electrode potential measurements of Vigouroux et al.

Ogawa and Murakami²⁹ used some of their alloys high in iron to check the electrode potential measurements of Vigouroux. They obtained a smooth potential composition curve from pure iron up to an alloy containing 18.38 per cent Zn, while with alloys higher in zinc no further change in the measured potential was observed. It was concluded that there was no evidence for the existence of either Fe_3Zn or Fe_5Zn , except that the latter composition would approximately represent the solid solubility limit of zinc in iron, which the authors placed at 18.38 per cent Zn.

It is well known today that reliable electrode potential measurements cannot be obtained unless the electrodes are physically and chemically homogeneous, and it seems very doubtful that the alloy electrodes prepared by any of the workers mentioned above could have had such uniformity. Moreover, the system being investigated, composed of iron, zinc, and either zinc sulfate or ferrous sulfate, is one that would cause considerable trouble in obtaining trustworthy measurements, as was admitted by Ogawa and Murakami. It is concluded that the results of the latter authors may be qualitatively correct, but that none of these electrode potential data should be given much weight.

Magnetic Properties of Iron-zinc Alloys

Raydt and Tammann³⁰ are the only workers who have attempted to prepare iron-zinc alloys by melting both constituents, the required temperature of over 1500° being attained in a bomb at pressures up to 130 atmospheres of hydrogen. By microscopic examination of etched alloys, they found that, in addition to FeZn_7 and FeZn_3 , the only phase high in iron was a solid solution of zinc in iron, and the solubility limit was placed by them at about 20 per cent, in good agreement with the later work of Ogawa and Murakami. No evidence was found for Fe_3Zn or

²⁷ F. Taboury: Reference of footnote 17.

²⁸ H. Le Chatelier: Reference of footnote 16.

²⁹ Y. Ogawa and T. Murakami: Reference of footnote 23.

³⁰ U. Raydt and G. Tammann: *Ztsch. anorg. Chem.* (1913) **83**, 257-266.

Fe_3Zn , as claimed by Vigouroux, or as somewhat doubtfully postulated by Guertler³¹ from a microscopic examination of galvanized iron specimens that had been polished at an angle to expose all the alloy layers.

The positive contribution by Raydt and Tammann was the initial determination of the gamma-alpha iron transformation temperature as a function of alloy composition, by means of magnetic permeability measurements. Reasonably pure zinc and iron were used in preparing the alloys. The magnetic transformation temperature decreased from about 785° for pure iron to about 647° for an alloy containing 33 per cent Zn, and then remained constant at $647 \pm 7^\circ$ from 33 to 74 per cent Zn. Although it is true that Raydt and Tammann prepared their alloys under very high pressures and hence might have obtained different alloy phases than would have been obtained at atmospheric pressure, still in determining the gamma-alpha iron transition it was necessary to anneal the alloys, and approximate equilibrium must have been obtained.

Ogawa and Murakami³² prepared a series of alloys containing from 30 per cent Fe up to pure iron, by heating together suitable amounts of a mother alloy and pure iron powder, and subjected these to magnetic, dilatometric, microscopic, chemical and electrode potential measurements. The X-ray measurements were reserved for a later paper, and the electrode potential measurements have already been discussed.

The magnetic analysis was carried out by taking heating and cooling curves on these alloys with an internal thermocouple and thus noting the temperature at which the magnetic intensity suddenly increased on cooling. These results seem to be somewhat more uniform than those of Raydt and Tammann, and for this reason are possibly to be preferred. Ogawa and Murakami found the curve of magnetic transformation temperature versus composition to be composed of two branches, and hence concluded that the break in the curve corresponded to the existence of a beta-iron phase, whose existence has not yet been established by direct experiment. The curve was found to become horizontal at 623° from about 25 to about 44 per cent Zn, and in conjunction with Raydt and Tammann's results it may be concluded that this line remains horizontal clear over to the vertical $\text{Fe}_3\text{Zn}_{10}$ boundary at 79.6 per cent Zn.

The Japanese authors obtained a partial check on the transformation temperature horizontal by carrying out thermal dilatation experiments on three alloys, a break in the thermal expansion curve being obtained at about 620° with alloys containing 29.8 and 22.4 per cent Zn, respectively, but none with a 14.6 per cent alloy.

It should be remarked that all the work that has been done on the magnetic transformation temperature has been done by means of cooling

³¹ W. Guertler: *Int. Ztsch. f. Metallographie* (1911) 1, 353-75.

³² Y. Ogawa and T. Murakami: Reference of footnote 23.

curves only, and that heating curves should also be obtained to determine whether or not the two methods would give identical results.

Lehmann³³ measured the magnetic susceptibility of alloys containing up to 8.5 per cent Fe; and obtained a sharp maximum in the susceptibility-concentration curve at 7.29 per cent Fe. This must be taken to correspond either to FeZn_7 saturated with Zn or to the hypothetical phase FeZn_{10} . Lehmann assumed the former, but it is difficult to explain the decrease in magnetic susceptibility as the iron content increases beyond the critical value, by either assumption. The shape of the susceptibility-concentration curve did not change when measurements were made at 160° . As with most of the experimental work on the iron-zinc system, the uniformity of the alloys prepared by Lehmann is open to question.

X-Ray Measurements

Osawa and Ogawa³⁴, using the alloys prepared by Ogawa and Murakami, compared the X-ray patterns obtained therefrom with the patterns produced by phases of known crystal structure in the Cu-Zn, Au-Zn and Ag-Zn systems (previously correlated by Westgren and others) and concluded that the phase previously known as FeZn_8 was in reality $\text{Fe}_3\text{Zn}_{10}$, was body-centered cubic in structure with 52 atoms per unit cell, and had a lattice parameter of 8.930\AA . The phase designated as FeZn_7 was identified as such and found to possess a close-packed hexagonal structure like that of zinc, in which the presence of iron had reduced the axial ratio from 1.86 for zinc to about 1.6 for an alloy containing 10.7 per cent Fe.

By measuring the lattice constant for a series of high-iron alloys, it was established that solid solution of zinc in the cubic iron lattice causes an expansion that reaches a maximum at about 18.38 per cent Zn; this value, therefore, is thought to represent the solid solubility of zinc in iron at ordinary temperature.

These three phases, together with zinc, were all that were found by X-ray examination. Anticipating the work of Stillwell and Clark, to be discussed in the next paragraph, it should be said that since the alloy lowest in iron used by Osawa and Ogawa contained 10.7 per cent Fe, they could not have detected the FeZn_{10} phase reported by Stillwell and Clark.

Stillwell and Clark³⁵ examined by a reflection method the X-ray structures exhibited by hot-dip galvanized steel wires and sheets, by progressively etching off layers of zinc about equal to the depth of penetration of the X-rays. In this way a series of patterns was obtained as a function of the thickness of the coating, and the relative amount of each crystal

³³ E. Lehmann: *Phys. Ztsch.* (1921) **22**, 601-03.

³⁴ A. Osawa and Y. Ogawa: *Ztsch. fur Kristallographie* (1928) **68**, 177-88.

³⁵ C. W. Stillwell and G. L. Clark: Reference of footnote 12.

type could be estimated. The results were slightly different for the wire and sheet, as follows:

The wire was galvanized with high-grade zinc and was subjected to a brief anneal after leaving the galvanizing bath. X-ray examination showed:

1. No solid solution of Zn in Fe next to the steel base.
2. The inner alloy layer is $\text{Fe}_3\text{Zn}_{10}$, not FeZn_3 .

3. The outer layer contained FeZn_7 , a solid solution of Zn in FeZn_7 , a solid solution of Fe in Zn (*sic*), and a phase with a body-centered cubic lattice, the composition of which was not determined, but which was most abundant near the outer zinc layer. On the basis of some chemical and microscopic studies by Schueler, whose work will be referred to later, the authors suggested that this phase might be FeZn_{10} .

The Armco sheet steel was galvanized with Prime Western zinc containing about 1.0 per cent of lead, and 0.3 per cent of cadmium. It showed:

1. No solid solution of Zn in Fe.
2. No evidence of $\text{Fe}_3\text{Zn}_{10}$.

3. The intermediate layers were composed chiefly of a solid solution of Zn in FeZn_7 , and the unidentified body-centered cubic phase, the latter being more concentrated near the surface.

4. A surface coating of pure zinc showing preferred orientation.

The most serious criticism of the work of Stillwell and Clark is concerned with their claimed detection of an altered zinc lattice produced by the solid solution of iron in zinc. It has been known for years that the solubility of iron in zinc is at most of the order of a few hundredths of a per cent; the results reported in the present paper indicate that even at 400° the solid solubility is not over 0.0028 per cent Fe, and moreover, that no alteration of the lattice constants of zinc can be detected by X-ray analysis of zinc containing up to 0.01 per cent Fe, provided true equilibrium has been attained by prolonged annealing.

Stillwell and Clark did not obtain complete data on the body-centered cubic material assumed to be FeZn_{10} and hence could not thus assign that formula to it; their conclusion was based on the location of the material near the outer boundary of the coating and upon Schueler's³⁶ attempt at chemical isolation and analysis. Such material seems never to have been found in microsections of galvanized coatings, although it might be expected to possess different etching characteristics from the adjacent FeZn_7 crystals which are hexagonal in structure. It is not felt that Stillwell and Clark have done more than to emphasize the necessity of a careful X-ray study of the zinc-rich phases under truly equilibrium conditions.

³⁶ J. L. Schueler: *Trans. Amer. Electrochem. Soc.* (1925) **47**, 201-226.

Ekman³⁷, a student of Westgren's³⁸, prepared several iron-zinc alloys for X-ray analysis by mixing the pure metal powders, packing them into small quartz tubes which were then sealed off in vacuo, fusing the samples (of about one gram each), annealing for several days at 700°, recrystallizing at 500° and quenching.

Ekman agreed with Osawa and Ogawa in finding that the phase formerly called FeZn_3 may be represented as $\text{Fe}_3\text{Zn}_{10}$, corresponding to a maximum iron content of 23 atomic per cent, that the crystals are body-centered cubic and contain 52 atoms per unit cell. However, Ekman obtained a much larger value for the lattice parameter than did the Japanese authors, 8.992Å. instead of 8.930Å. Ekman showed, by finding evidence of a variable lattice parameter, that this phase existed over a range of composition, thus indicating that some adjacent material richer in zinc, probably FeZn_7 , was soluble in it. Ekman attempted to extrapolate his measurements so as to show that the true formula of the phase was probably $\text{Fe}_3\text{Zn}_{21}$, at 19 atomic per cent Fe, and that the range of composition up to 23 atomic per cent would then be obtained by solution of a phase richer in iron. It appears that this was done in the hope of making this alloy correspond to a principle established by Westgren, that many alloy systems possess body-centered cubic phases to which such a formula can be assigned; the principle is that the ratio of the number of valence electrons to the number of atoms per unit cell shall be as 21:13, and that it is necessary to assign zero valence to elements, such as iron, which are part of a transition group of the periodic system. This is a specific application of the Hume-Rothéry rule. Ekman's data do not appear to support his conclusions, however, and it is thought that all of the X-ray data to date indicate that $\text{Fe}_3\text{Zn}_{10}$ is the correct formula for this phase.

Structure of Galvanized Coatings

Most of the remaining papers on the alloys of iron and zinc have to do with the phases present in galvanized iron coatings. There are in addition a large number of papers reporting the composition of the iron-zinc dross found in galvanizing pots, but these results are at best only qualitative since it is not possible to obtain the crystals free from zinc.

The work of Schueler³⁶ will be discussed first, since it is in a way related to that of Stillwell and Clark. Schueler's paper is a description of the then new process of galvannealing and of the structure of the coatings thus produced, which contain very little free zinc but consist mostly of various alloy layers. These coatings were examined microscopically, and were analyzed chemically by a stripping method in which coated

³⁷ W. Ekman: *Ztsch. phys. Chem.* (1931) **12B**, 57-78.

³⁸ A. Westgren: *Svensk. Kem. Tids.* (1930) **42**, 193-204.

wires were subjected to successive periods of from 10 sec. to 1 min. in a sulfuric acid stripping bath, up to the 15 min. necessary to remove the entire coating. Each solution so obtained was analyzed for iron, and the corresponding loss in weight of the wire was determined. Thus an approximate picture was obtained of the iron content of the coating as a function of the thickness of the coating. Among the several layers present one was found to have approximately the composition of FeZn_{10} (about 7.5 per cent Fe) and this formula was assigned to it by Schueler without, however, obtaining microscopic identification of this phase.

Rigg³⁹ has described an interesting experiment in which clean surfaces of zinc and iron were pressed together and kept for various times at elevated temperatures below the melting point of zinc. He finds the interesting result that the iron appears to diffuse into the zinc rather than vice versa, as might have been expected. By chemical and/or physical separation and analysis of the various layers thus formed, Rigg concluded that two well defined layers of diffusion products were formed; a layer of about 0.08 mm. constant thickness next to the iron base that contained about 17 per cent Fe, and a thicker layer outside this, which contained from 0–11 per cent Fe. On continued heating the thin layer moved toward the zinc, being continuously converted into the zinc-rich layer; this was taken to indicate that the principal diffusing constituent was the iron.

The photomicrographs presented by Rigg are not well enough prepared nor sufficiently magnified to make positive identification possible, but there is occasionally evidence of one more alloy layer than is usually found in galvanized coatings.

Tammann and Rocha⁴⁰ prepared some specially galvanized iron sheets by dipping them into pure zinc and holding them for a given length of time before withdrawing them. Thus, they used a series of different times and temperatures, and then measured, microscopically, the thickness of the various alloy layers. They found, in general, three distinct alloy layers, whereas normally only two alloy layers are found on galvanized iron. In one experiment, in which the specimen was given a subsequent anneal, they showed a photomicrograph exhibiting four alloy layers, the inner one developed by the anneal being assumed to be a solid solution of zinc in iron. If Tammann and Rocha's findings are correct, space must be provided on the equilibrium diagram for an additional alloy phase; the authors concluded that it should lie between $\text{Fe}_3\text{Zn}_{10}$ (FeZn_3) and the alpha-iron phase.

Schueler and also Stillwell and Clark indicate that there may be another phase richer in zinc than FeZn_7 . Some years ago⁴¹ The New

³⁹ G. Rigg: *Jnl. Inst. Metals* (1934) **54**, 183–192.

⁴⁰ G. Tammann and H. I. Rocha: *Ztsch. anorg. Chem.* (1931) **199**, 299–301.

⁴¹ W. H. Finkeldey: *Proc. Amer. Soc. Test. Mat.* (1926) **26**, pt. II, 304–316.

Jersey Zinc Co. carried on an extensive investigation of hot-dip galvanizing, in the course of which hundreds of galvanized specimens, produced under controlled conditions, and some of them having subsequent annealing treatments, were examined microscopically. In all these experiments there was occasionally slight evidence, but no positive proof, of the existence of another alloy layer in addition to those now known to be: (1) zinc, (2) FeZn_7 , (3) $\text{Fe}_3\text{Zn}_{10}$, (4) iron. The metallographic technique has been greatly improved in the past 10 years, and it is possible that microscopic and X-ray examination of carefully galvanized specimens, or of electrogalvanized and annealed specimens, might give more information about the existence of additional constituents. For the present, however, it must be concluded that there is no conclusive evidence of the existence of a phase such as FeZn_{10} , and that it must be assumed that iron-zinc alloy crystals having the composition of about 7.3 to 7.8 per cent Fe consist of FeZn_7 with zinc in solid solution.

Ogawa and Murakami included several photomicrographs in their paper, some of which seem to indicate that the gamma-iron solution breaks down by means of a eutectoid reaction. If true, this would necessitate some alteration in the present tentative construction of the high-iron end of the diagram. This part of the diagram, as given in Fig. 9, was taken without modification from the paper of Ogawa and Murakami, and while it is almost certainly incorrect except for the magnetic transformation lines, any change therein should be based on experimental data.

When Guertler⁴² published his paper in 1911 on the structure of galvanized iron coatings it contained some new and interesting information, together with photomicrographs of typical alloy structures. Guertler also attempted to arrange the various alloy layers in the order of relative electrolytic solution potentials, but his chemical evidence would be considered faulty today. Later⁴³, he said that he had found evidence of another alloy phase (in addition to FeZn_7 and FeZn_3) in galvanized coatings.

Numerous other papers are indirectly related to the formation of iron-zinc alloys, but none of them seem to have any direct bearing on the establishment of the iron-zinc equilibrium diagram. Reference to many of these papers will be found in Mellor's recent treatise on iron⁴⁴.

SUMMARY

This summary of the present status of the iron-zinc equilibrium diagram includes the experimental work reported in Part I of this paper

⁴² Reference of footnote 30.

⁴³ W. Guertler: *Handbuch d. Metallographie*, 1, pt. 1, 430-444. 1912.

⁴⁴ Mellor: *Comprehensive Treatise of Inorganic Chemistry*, 13, 543-45. New York, 1934. Longmans, Green & Co.

as well as that of earlier workers. The various phase boundaries mentioned in this summary are lettered according to the scheme used in the preparation of the phase equilibrium diagram shown in Fig. 9.

1. The liquidus curve (*ACG*) has been redetermined and found to lie considerably nearer the zinc boundary than was indicated by earlier results.

2. The solid solubility of iron in zinc (shown in the enlarged portion of the diagram) has been found to be between 0.0009 and 0.0028 per cent Fe.

3. The eutectic temperature has been fixed at 419.4° C. The eutectic composition has been determined to lie at about 0.018 per cent Fe.

4. The solid solubility of zinc in iron (lines *YLKJ*) appears from the literature to be about 18 per cent in alpha iron at room temperature, and about 26 per cent in gamma iron at about 625° C. However, the solubility of zinc in iron as a function of temperature is without experimental foundation.

5. The peritectic horizontals *CDE* and *GH-J* have been quite accurately fixed at 672° and 782°, respectively, by means of differential heating-curve arrests.

6. The magnetic transformation temperature as a function of the zinc content of iron-zinc alloys has been determined by earlier workers (lines *PNMKF*); it is constant from about 20 to about 70 per cent Zn, and hence probably along the entire line *KF*. The magnetic transformation horizontal is variously given at 647° and 623°, the latter value being preferred. The shape of the magnetic transformation curve *KMNP* indicates the possible existence of a beta-iron phase *PRN*, which has not been searched for as yet.

7. The existence of a phase having the composition of FeZn_{10} (near line *SB*) has been suggested anew by some recent X-ray work, but the composition of this phase was not determined, and there has been no microscopical, thermal, or additional X-ray verification of its existence.

8. The phase having the composition corresponding to FeZn_7 (line *TD*) has been identified by others and found to have a close-packed hexagonal structure similar to that of zinc, in which the axial ratio of 1.86 for the zinc lattice has been decreased to about 1.6 by the presence of iron. There is evidence that zinc is soluble in FeZn_7 , thus providing for the range of homogeneous composition of the latter extending from 10.9 probably to about 7.3 per cent Fe. The remaining phase boundary (*SBD*) has not been experimentally established as yet.

9. The phase originally designated as FeZn_3 has been found by X-ray measurements reported by three recent workers to correspond closely to the formula $\text{Fe}_3\text{Zn}_{10}$ (line *VH*), to have a body-centered cubic structure containing 52 atoms per unit cube, and a lattice parameter of 8.962 to

8.992Å. This variable cube size is evidence that this phase also is homogeneous over a range of composition, but the extent of the latter has not been completely determined. Indications are that at least one other phase, probably FeZn_7 , must be soluble in $\text{Fe}_3\text{Zn}_{10}$. The broken line *UEH* in Fig. 9 indicates a possible boundary for this phase. On the other hand, cooling-curve arrests have been reported along the portion of the 672° peritectic horizontal *EI*, and eventually a choice will have to be made between the two methods of constructing this portion of the diagram.

10. No reliable evidence has been presented to indicate the existence of any additional phase or phases having a composition between that of $\text{Fe}_3\text{Zn}_{10}$ and that of a solid solution of zinc in iron. This portion of the alloy system (*WFKLY*) is in need of examination, and at present is considered to be a mixture of the two phases mentioned.

DISCUSSION

(*Samuel L. Hoyt presiding*)

S. TOUR,* New York, N. Y.—Some years ago, I did some work on zinc alloys high in iron, and I found a peculiar change in volume on annealing. I wonder whether the authors of this paper made any dilatometric studies or volume-change studies at these peritectic regions. In a zinc-iron alloy containing considerable portions of $\text{Fe}_3\text{Zn}_{10}$. I found on heating at around 1100° F., which would be in the neighborhood of one of the peritectic regions shown in this paper, an increase of volume of something of the order of 20 per cent. This question of volume changes of the high-iron constituent may have considerable practical application in galvanized iron.

E. A. ANDERSON,† Palmerton, Pa.—In this particular investigation no work was done on the volume changes. We have noted repeatedly in the formation of FeZn_7 that there is a rather large expansion. We ruined a number of nice pieces of equipment by allowing the temperature to get a little too low and the expansion cracked the equipment. Some time ago, we became interested in determining whether that expansion meant the production of a lattice of low density, or the production of voids in the casting. We made a direct density determination on some of this FeZn_7 material, and found it to check very closely with the density calculated by the rule of mixtures, and the conclusion was that the expansion is due to the production of voids in some unknown manner, and not to the production of a lattice of low density. We have no immediate plans for doing any volumetric work on that point.

K. R. VAN HORN,‡ Cleveland, Ohio.—Mr. Anderson indicated that there was not conclusive evidence of the existence of a eutectic. The microstructures were not definite and the lowering of the melting point of zinc could not be positively detected by thermal methods. Therefore, as the lowering and consequent eutectic formation has not been definitely ascertained, it is possible that there might be a slight elevation of the melting point of zinc with the addition of iron. This might be explained by peritectic reaction in which the zinc solid solution containing iron reacted with the

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† Metallographist, New Jersey Zinc Co. In the absence of the authors, Mr. Anderson presented the paper.

‡ Research Metallurgist, Aluminum Company of America.

melt to form pure zinc, rather than the expected formation of zinc reacting with liquid to form a new compound, which would have been readily observed microscopically by the authors. Such a condition, attributable to a discontinuous solid solution, would give two thermal arrests, very close together, which would converge at 100 per cent zinc. In the literature there are three or four alloy systems that have a nearly constant solid solubility over a range of temperature, and in which the base metal reacts with a liquid to form a solid solution of the added element in the base metal. These examples are characterized by systems of extremely low solid solubility from a few thousandths of 1 per cent at lower temperatures, to hundredths of 1 per cent at the peritectic temperature. This similarity to the iron-zinc system occasioned the remarks.

Metallographic proof of the proposed hypothesis would be evidenced by coring. However, such coring is generally not easily detected, and is revealed only by unusual polishing and etching methods (electrolytic). Of course, if the authors obtain a definite lowering of the melting point with the addition of iron, this system would be of the eutectic type.

One additional question: Do the alloys exhibit room-temperature aging? If so, this might explain some of the variations in the electrical conductivity measurements.

E. A. ANDERSON.—The point that Mr. Van Horn brings up about the possible existence of a rather unique type of peritectic can be answered simply in this way: we have never seen indications of coring in pure zinc of relatively high iron content. That does not say that it may not be there, but it would be a rather difficult task to determine its existence.

These alloys were heat-treated and subjected to examination within a few hours after they were removed from the quenching vat. There would hardly be time for appreciable change. Studies extending over a long period of time have indicated that while iron diffuses rapidly in zinc the rate is sufficiently slow to permit examination after quenching.

K. R. VAN HORN.—The measurement of the electrical conductivity within three or four hours does not necessarily indicate that room-temperature aging could not have occurred previous to the determination. A series of the alloys of a binary aluminum system have precipitated before electrical conductivity measurements could be made. That is, there was so much precipitation between the quenching of the specimen and the attainment of equilibrium at 25° C. in the measuring apparatus (consuming about one minute) that values were useless for the determination of the solid solubility. The electrical conductivity values of these alloys also varied with the time of aging at room temperature for a considerable period of time, such as two days. It can be seen, therefore, that the time of aging at room temperature affects the electrical conductivity of these alloys. This system is unusual, as the electrical conductivity of most alloys generally can be determined immediately or after a few days with little or no change in the values.

S. L. HORT,* Milwaukee, Wis.—In maintaining molten zinc in a galvanizing pot, there seems to be sort of a dead-line temperature above which you should not go if you wish to preserve your galvanizing pot. I should like to ask Mr. Anderson to discuss that particular point from the point of view presented in this paper, if that is a feasible thing to do. Just what is that limiting temperature due to? Is it simple?

E. A. ANDERSON.—I think there is a relatively simple answer to that. In a quiescent system of that sort, there is compound formation immediately adjacent to the iron wall, and it becomes a question of the diffusion rate through that layer of compound. As the temperature is increased a critical temperature is reached at which the diffusion rate becomes relatively rapid and the compound layer gets thinner and thinner, and the attack on the iron suddenly increases at a rapid rate. I would not say

* Research Metallurgist, A. O. Smith Corporation.

that that explanation would stand the test of a rigid investigation, but it is entirely reasonable.

This present work represents the equilibrium condition; the condition you describe is a dynamic condition that is continually changing.

C. W. STILLWELL,* Framingham, Mass. AND G. L. CLARK,† Urbana, Ill. (written discussion).—The more precise definition of the iron-zinc system which has been established in this paper is doubtless of great value. Without question the authors' evidence that there is no detectable difference in the lattice dimensions of pure zinc and of the saturated solid solution of iron in zinc is correct, and to consider our numerical results as conflicting evidence is to read into them a degree of accuracy that was never intended. The main purpose of our investigation, as stated in our paper⁴⁵, was to determine qualitatively the several iron-zinc phases in a galvanized coating, not to establish precise lattice dimensions. In this connection we proposed, as the present authors have done in commenting upon our paper, the further careful study of the zinc-rich portion of the system in order to establish the identity of the body-centered cubic phase, which we suggested might be FeZn_{10} . Contrary to the present authors, however, we still feel, as we suggested originally, that this may be a metastable phase, which will not be found in the alloy in true equilibrium at room temperature.

The authors' apparent skepticism regarding the proposed formula $\text{Fe}_3\text{Zn}_{21}$ for the phase usually written $\text{Fe}_5\text{Zn}_{10}$ is interesting. It is by no means an established fact that the alloys of the transition elements follow the Hume-Rothery rule. To make them follow, it is necessary to assign zero valence to the transition element; and this raises certain inconsistencies. Assigning a zero valence to palladium, for example, so that the compound $\text{Pd}_5\text{Zn}_{21}$ prepared by Ekman will fit the ration, 21 valence electrons to 13 atoms, means that the beta phase CuPd cannot satisfy the ratio 3:2, which is characteristic of all beta phases. Zintl and Brauer⁴⁶ have proposed that the Hume-Rothery rule applies only to alloys in which true metallic bonds predominate; and that when there is an appreciable contraction in atomic volume (3 to 8 per cent in the group of gamma phases described by Ekman), indicative of polarization influences, the rule should not be expected to hold. At present, therefore, there is not sufficient evidence to justify the elimination of the formula $\text{Fe}_5\text{Zn}_{10}$ in favor of $\text{Fe}_3\text{Zn}_{21}$.

E. C. TRUESDALE, R. L. WILCOX AND L. J. RODDA (written discussion).—With regard to Dr. Van Horn's suggestion and explanation of a possible peritectic reaction as an alternative to the proposed eutectic, the authors still feel that, of the two, the eutectic construction is the more probable one, on the basis of the available evidence. As to the possibility of aging occurring at room temperature, the authors would like to emphasize that the solid solubility of iron in zinc appears to be independent of temperature at least down to 150°C ., and they feel that any precipitation of iron (asFeZn_7) from there down to room temperature must be of a very low order of magnitude, and even if it occurs cannot entirely account for the peculiar shape of the electrical conductivity curve.

The authors thank Dr. Stillwell and Professor Clark for their suggestion regarding the possible existence of FeZn_{10} as a metastable phase, and for their further elucidation of the question of the composition of the gamma-type phase ($\text{Fe}_3\text{Zn}_{10}$ as against $\text{Fe}_5\text{Zn}_{21}$). Both of these points illustrate the feeling of the authors, which they tried to emphasize in Part II of the paper, that all of the solid phases of the iron-zinc system are in need of further careful study, and that the facts regarding an alloy system should be ascertained before a too serious attempt is made to make the system fit a rule.

* Dennison Manufacturing Co.

† University of Illinois.

⁴⁵ Reference of footnote 12.

⁴⁶ Zintl and Brauer: *Ztsch. phys. Chem.* (1933) 20B, 245.

Phase Changes during Aging of Zinc-alloy Die Castings, II—Changes in the Solid Solution of Aluminum in Zinc and Their Relation to Dimensional Changes

BY M. L. FULLER* AND R. L. WILCOX,* JUNIOR MEMBERS A.I.M.E.

(Chicago Meeting, October, 1935)

Most commercial alloys undergo changes in phase composition after casting. This is a natural result of the fact that the alloys are not in a state of phase equilibrium as cast and phase changes will therefore take place, with more or less rapidity, in an attempt to attain equilibrium.

The practical aspect of aging in zinc-alloy die castings concerns the changes in physical properties and in dimensions that may accompany aging phase changes. Harmful alterations have been reduced to a minimum and zinc-alloy die castings are being produced today that are so stable with respect to dimensions and physical properties that they are entirely suitable for most practical purposes¹.

In the first paper² of this series, and in this paper, aging phase changes of zinc-alloy die castings have been investigated and the possible influence of these changes on dimensional changes of the castings has been evaluated and compared with the dimensional changes actually experienced. The change of dimensions has been selected for practical comparison in these papers because the effect of phase changes on the dimensions of a casting is directly calculable from X-ray crystal-analysis data of the phase structure.

The die-casting alloys considered contain, in addition to zinc, 4 per cent of aluminum, about 0.03 per cent magnesium, and from 0 to 3 per cent of copper. It was shown in the former paper that the eutectoidal decomposition of the beta aluminum-zinc phase, while intrinsically capable of causing a considerable shrinkage, can have very little effect on the observed shrinkage of die castings because it takes place within a few days of aging, whereas the observed shrinkage continues for five weeks. It was therefore concluded that the other existing phase change, namely, the segregation of secondary phase from the zinc-base solid solution, must account for the major portion of the shrinkage.

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¹ E. A. Anderson and G. L. Werley: *Metals & Alloys* (1934) **5**, 97.

² M. L. Fuller and R. L. Wilcox: *Trans A.I.M.E.* (1935) **117**, 338.

This paper reports the results of an extensive investigation of aging changes in the α ³ solid solution of aluminum in zinc in the copper-free zinc alloy (A.S.T.M. No. 23 alloy; 4 per cent Al, 0.04 per cent Mg, remainder high-purity zinc 99.99+ per cent). X-ray and microscopical examination show the course of the phase changes. From the X-ray crystal analysis data are calculated the dimensional changes that would be expected to take place in the casting as a result of the phase changes. These calculated dimensional changes are compared with the actual changes that took place.

It is demonstrated that the actual dimensional changes that occur during normal aging are accounted for in a semiquantitative way by the changes in the α phase, and therefore, in this alloy the β transformation contributes very little, if any, to the shrinkage experienced.

The effects of various low-temperature annealings, such as commercial stabilizing annealings, have also been investigated and reported in this paper. An estimate of the composition of the α phase in each specimen examined has been made on the basis of lattice dimension measurements. An approximation of the solid solubility of aluminum in zinc at various temperatures has been made and the data are given.

EXPERIMENTAL

Alloys.—A commercial zinc die-casting alloy having the following composition was used in this work:

4.1 per cent aluminum	0.001 per cent tin, maximum
0.04 per cent magnesium	0.075 per cent iron, maximum
0.004 per cent lead, maximum	0.03 per cent copper, maximum
0.004 per cent cadmium, maximum	

The die-cast test specimens were prepared under conditions simulating good commercial practice. Two separate lots were used, the first being cast in May, 1934, and the second in November, 1934. These two lots will be referred to as cast No. 1 and cast No. 2, respectively. For the dimensional-change measurements and most of the X-ray work, the specimens were $\frac{1}{4}$ in. square in cross section and 6 in. long, conforming with the A.S.T.M. specifications for a Charpy impact-test specimen (B-86-34T).

Dimensional-change Measurements.—Immediately after casting the ends of the test bars were milled to flat mutually parallel surfaces, in order to make possible precise measurement. Using micrometer calipers

³ Throughout this paper α will be used to designate the zinc-base solid solution, and γ to designate the aluminum-base solid solution.

and a special jig⁴ for holding the specimen, measurements to within 0.0002 in. in a 6-in. length were made.

X-ray Method.—The X-ray diffraction patterns were obtained by the back-reflection technic using X-radiation from a chromium target tube. Two separate specimens were examined for each condition studied.

CALCULATION OF DIMENSIONAL CHANGES FROM CRYSTAL ANALYSIS

The mean atomic volume of a crystalline phase is calculable from its lattice dimension and structure as derived from X-ray diffraction measurements. The cube root of the mean atomic volume may be called the mean atomic "length." Changes in the latter value, which result from changes in composition of the crystal, should be reflected in a directly proportional manner in the gross dimensions of a polycrystalline aggregate, such as a die casting. In zinc-base solid solutions, the changes in length in the individual crystals are not the same in all directions. The validity of the use of the "mean atomic length" is dependent upon the existence of a uniformly random orientation of the crystals of the casting.

When the composition of a crystalline phase is altered there is always an accompanying depletion or production of a secondary phase. Therefore, a rigorous calculation of gross dimensional changes from crystal-structure data must consider the relative amounts of at least two phases and the changes in mean atomic length of these phases.

Disregarding the role in the phase structure of the minor constituents of the alloy studied in this investigation, there exist two phases—alpha and gamma aluminum-zinc. Beta aluminum-zinc is probably completely decomposed⁵ before dimensional-change measurements can be made. The room-temperature aging of this alloy, as will be described later, results in the depletion of the aluminum content of the alpha phase from 0.35 to 0.05 weight per cent, the remainder of the aluminum being crystallized on the gamma lattice. Under these conditions, the volume percentage of the gamma phase changes from 8.5 to 9.0 per cent, by an approximate calculation.

It is evident that the exact calculation of the changes in mean atomic length requires a measurement of the lattice dimensions of both alpha and gamma in a given specimen and a knowledge of the lattice dimension-composition relationship for each phase. Since the diffraction lines of gamma are only infrequently recorded on the X-ray diffraction pattern of a zinc-alloy die casting, it becomes necessary to limit the calculation of dimensional changes to the principal phase, alpha. The omission of

⁴ For a description of this, see Zamak, *The Zinc Base Die Casting Alloy*. New Jersey Zinc Co. *Research Bull.*

⁵ M. L. Fuller and R. L. Wilcox: Reference of footnote 2.

the gamma phase from the calculation introduces no significantly increased error, however, because of the magnitude of the errors that are inherent in the measurement and calculation of the mean atomic length of the alpha phase.

In calculating the mean atomic volume (and length) of alpha, the dimensions of the unit hexagonal prism are derived directly from the 00.1 (4) and 10.0 (2) reflections and by simultaneous quadratic equations from the 11.2 and 10.4 reflections. The derivation of mean atomic lengths from measured interplanar spacings for hexagonal crystals, as compared to cubic crystals, involves a series of mathematical operations,

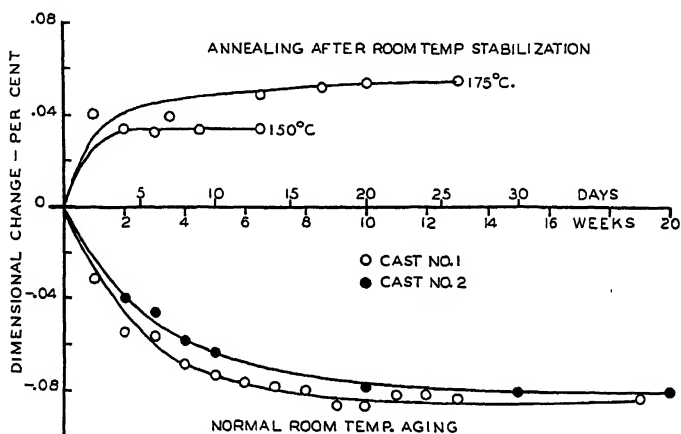


FIG. 1.—DIMENSIONAL CHANGES OF ZINC-ALLOY DIE CASTING. ROOM-TEMPERATURE AGING AND POST-AGING ANNEALING.

A.S.T.M. No. 23 alloy, 4.1 per cent aluminum, 0.04 per cent magnesium, remainder high-purity zinc (99.99+ per cent).

which frequently yield a distorted result depending upon the fortuitous disposition of the experimental errors in the original measurements. The quadratic equations involve the square root of the difference of the squares of two measured interplanar spacings. The calculation of mean atomic length involves the cube root of the cubic value obtained in calculating the volume of the unit cell. In cubic crystals, the mean atomic length is directly proportional to any measured interplanar spacing.

ROOM-TEMPERATURE AGING

After casting, the test specimens underwent a shrinkage that is graphically shown for the two separate casts in Fig. 1. On cast No. 2, X-ray examinations were made immediately after casting and after 5 and 17 weeks of room-temperature aging. Table 1 gives the shrinkage calculated from the X-ray data in comparison with the shrinkage actually experienced. In addition, the table gives the mean atomic volumes and lengths and the percentages of aluminum in the alpha phase for the

several conditions. The table also shows that room-temperature aging is accompanied by a decrease in the aluminum content⁶ of the alpha phase from 0.35⁷ per cent in the freshly cast material to 0.05 per cent in the fully aged material. The alpha phase in the freshly cast condition was obviously supersaturated with aluminum with respect to room-temperature equilibrium and during aging this supersaturation was relieved by the segregation of gamma and the depletion of the aluminum content of alpha. The change in aluminum content of alpha is naturally accompanied by a change in the lattice dimensions and hence in the mean atomic length. (The lattice dimensions are tabulated in the appendix to this paper.)

TABLE 1.—*Room-temperature Aging, Cast No. 2*

Treatment	Weight Per Cent Al in Alpha	Mean Atomic Volume, Å. ³	Mean Atomic Length, Å.	Change in Length, Per Cent	
				Calculated	Actual
As cast	0.35	15.173	2.4757	Datum	Datum
5 wk. room temp..	0.13	15.140	2.4739	-0.074	-0.063
17 wk. room temp.	0.05	15.130	2.4733	-0.097	-0.080

Table 1 gives the theoretical dimensional changes, calculated according to the procedure described earlier in the paper. It is not possible to make an exact quantitative comparison between the actual and calculated changes in length, for two reasons: (1) The calculated values may be in error by as much as 20 per cent, owing to errors in the experimental measurement of the interplanar spacings of the alpha phase; (2) it is not definitely established that the castings can conform exactly in length with the changes of their component crystals.

The important fact shown is that the actual change of dimensions is in the same direction and of the same order of magnitude as that which is calculated to be due to the change in composition of the alpha phase. This confirms in a semiquantitative way the theory expressed in the previous paper on the beta-phase decomposition, that the latter can account for only a small portion of the aging shrinkage.

The ideal situation would be to calculate with greater precision the dimensional change due to the segregation of gamma from alpha and to measure with exactness the change in actual density of the casting. The

⁶ The data upon which the aluminum contents of the alpha phase are estimated are appended to this paper.

⁷ Not all freshly die-cast specimens of this alloy have an aluminum content of the alpha phase of 0.35 per cent. The X-ray examinations of other casts, both laboratory and commercial, have shown that variations in the casting conditions and manner of handling after casting will vary this initial value.

difference between the calculated change due to alpha and the actual change could then be ascribed to the beta decomposition.

The attainment of this ideal, from a crystal analysis standpoint, is made impossible by the lack of uniformity among the alpha crystals in die castings. This is evident from the X-ray patterns, since the diffrac-

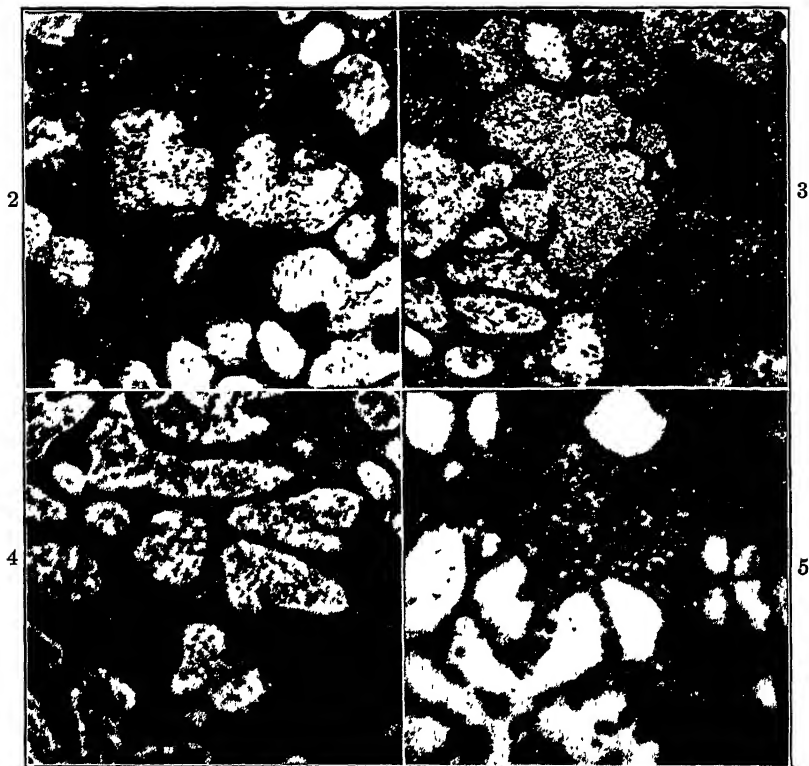


FIG. 2.—CAST No. 1, ONE DAY AFTER CASTING. $\times 1000$, WITH PRIMARY ALPHA GRAINS IN FOCUS (LARGE WHITE GRAINS).

FIG. 3.—CAST No. 1, TEN WEEKS AFTER CASTING. $\times 1000$, WITH PRIMARY ALPHA GRAINS IN FOCUS (LARGE WHITE GRAINS).

FIG. 4.—CAST No. 1, 19 WEEKS AT ROOM TEMPERATURE, 13 DAYS 150° C. AND QUENCHED. $\times 1000$.

FIG. 5.—CAST No. 1, 18 WEEKS AT ROOM TEMPERATURE, 35 DAYS 175° C. AND QUENCHED. $\times 1000$.

A.S.T.M. alloy No. 23, 4.1 per cent aluminum, 0.04 per cent magnesium, remainder high-purity zinc (99.99+ per cent).

tion lines are not as sharp as they would be for crystals of uniform composition. Further evidence for this is shown by microscopical examination.

Figs. 2 and 3 show the microstructures of the die casting in the freshly cast condition and after 10 weeks of room-temperature aging, respectively. The structures show large white patches of primary alpha and a fine-grained alpha-beta eutectic mixture. (The beta of the eutectic has decomposed eutectoidally into alpha and gamma.) Such a structure

is not likely to have a uniform composition among the individual crystals of alpha. In confirmation of the X-ray evidence, the photomicrographs show that aging causes gamma to segregate from the alpha phase. Some segregation is evident in the original photomicrographs taken one day after casting.

SUBEUTECTOIDAL ANNEALING AFTER ROOM-TEMPERATURE STABILIZATION

Previous to this investigation, it had been shown by Anderson and Werley, of this laboratory, that the annealing of castings that had been aged at room temperature produced an expansion. From the fact that such expansion could be produced by annealing at temperatures below the beta eutectoidal temperature (270° C.), it was deduced that the beta phase could have no influence on the expansion.

In order to determine the cause of this expansion in the present investigation, fully aged and dimensionally stabilized castings were annealed until dimensional stability was reached at 150° and 175° C. The course of the expansion was determined by periodically removing the specimens from the annealing furnace, quenching them to room temperature, measuring their lengths and returning to the annealing furnace, etc., until dimensional stability was reached. The expansion data are shown in Fig. 1. X-ray examination disclosed that redissolution of the gamma into alpha had taken place. Table 2 shows that the aluminum content of alpha increased from 0.04 to 0.17 per cent at 150° C. and from 0.04 to 0.28 per cent at 175° C. The actual expansion that took place is accounted for by that calculated to be due to the change in the alpha phase, within the limits of error.

TABLE 2.—*Subeutectoidal Annealing after Room-temperature Stabilization, Cast No. 1*

Treatment	Mean Atomic Volume, Å ³	Mean Atomic Length, Å.	Weight Per Cent Al in Alpha	Change in Length, Per Cent	
				Calculated	Actual
Stabilized at room temp.	15.129	2.4733	0.04	Datum	Datum
Stabilized at 150° C.*....	15.147	2.4742	0.17	+0.037	+0.033
Stabilized at 175° C.*....	15.161	2.4750	0.28	+0.068	+0.055

* Originally stabilized at room temperature.

The photomicrograph of Fig. 3 is representative of the structure of the specimens prior to the annealing treatments. Figs. 4 and 5 show the structures after annealing at 150° and 175° C., respectively. The redissolution of gamma (black grains) into alpha is strikingly evident on these photographs. It is interesting to note that the large white grains of

alpha are substantially free from gamma after the 175° C. annealing. It is evident from these data and from the data of the preceding section (on room-temperature aging) that change in the alpha phase is the chief cause of the dimensional alterations experienced in aging and heat-treating die castings of this alloy. The fact that expansion equivalent to the shrinkage of aging can be produced by subeutectoidal annealing, which can affect nothing but the alpha-gamma relationship, makes the role of the beta-phase decomposition in aging shrinkage seem to be very minor indeed.

COMMERCIAL STABILIZATION ANNEALING

A commercial procedure for hastening the aging shrinkage of zinc-alloy die castings requires the annealing of the castings for about three

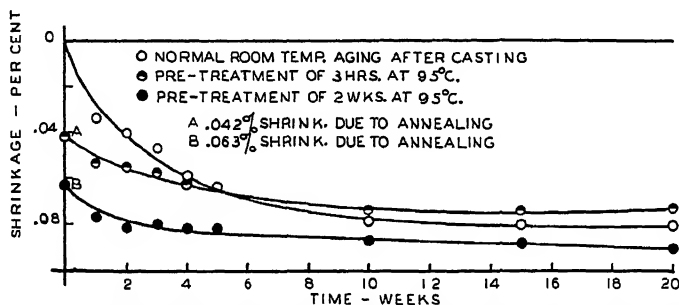


FIG. 6.—NORMAL AGING AND AGING AFTER STABILIZATION ANNEALINGS.

A.S.T.M. No. 23 alloy, 4.1 per cent aluminum, 0.04 per cent magnesium, remainder high-purity zinc (99.99+ per cent).

hours at 95° C. soon after casting. Generally, the major portion of the shrinkage takes place during this annealing. After the annealing, a small amount of further shrinkage takes place during room-temperature aging.

In order to determine the mechanism of aging under these conditions, the X-ray method was again applied. The experiment was carried further by annealing a separate group of freshly cast specimens for a period long enough to insure dimensional stability at 95° C. In each specimen room-temperature aging following the annealing was studied.

Fig. 6 and Table 3 are based on the data obtained. Cast No. 2 was used in these experiments; this cast showed an aluminum content of alpha of 0.35 per cent in the freshly cast condition. These data show that the changes in the alpha phase again account for the shrinkage experienced. It is interesting to see that the extent of the aluminum depletion in alpha was greater by aging after the longer annealing of 2 weeks at 95° C. than the shorter annealing of 3 hr. at 95° C., indicating that equilibrium at room temperature was more nearly approached. The calculated shrinkages are the same within the limits of error for the

six conditions. The course of the composition changes in the alpha phase seems to be a more sensitive indication of the progress of aging than the calculated shrinkage values. The actual shrinkage after the 3-hr. annealing was very much less than that which was calculated.

TABLE 3.—*Commercial Stabilization Annealing, Cast No. 2*

Treatment	Weight Per Cent Al in Alpha	Mean Atomic Volume, A. ³	Mean Atomic Length, A.	Change in Length Per Cent	
				Calculated	Actual
As cast... ..	0.35	15.173	2.4757	Datum	Datum
3 hr. 95° C.	0.13	15.137	2.4737	-0.082	-0.042
5 wk. room temp. ^a	0.07	15.134	2.4735	-0.088	-0.063
19 wk. room temp. ^a	0.07	15.140	2.4739	-0.073	-0.073
As cast.....	0.35	15.173	2.4757	Datum	Datum
2 wk. 95° C.	0.08	15.131	2.4734	-0.093	-0.063
5 wk. room temp. ^b	0.06	15.132	2.4734	-0.093	-0.082
15 wk. room temp. ^b	0.04	15.135	2.4736	-0.085	-0.088

^a Originally annealed 3 hr. at 95° C. immediately after casting.

^b Originally annealed 2 wk. at 95° C. immediately after casting.

Evidently, in this case, the castings failed to conform in gross dimensions as rapidly and to the same extent as the changes occurred in the individual crystals.

SUMMARY

The dimensional changes that occur in zinc-alloy die castings (A.S.T.M. alloy No. 23) during aging and low-temperature annealings have been shown to be due to changes in the alpha phase. These changes are the segregation from, or the redissolution of gamma in, the alpha phase. This relationship has been established semiquantitatively by a comparison of dimensional changes calculated from X-ray data on the phase structure with those changes actually experienced. The evidence indicates strongly that the beta-phase decomposition plays a minor part, if any, in the aging shrinkage of this alloy. The particular findings were as follows:

1. Room-temperature aging of freshly cast material resulted in a segregation of gamma from alpha and an accompanying shrinkage.
2. The annealing at 150° and 175° C. of castings that had been dimensionally stabilized at room temperature resulted in the redissolution of gamma into alpha and a corresponding expansion.
3. Commercial stabilizing annealing of 3 hr. at 95° C. resulted in a more rapid depletion of the aluminum content of alpha than takes place during room-temperature aging and a correspondingly more rapid

shrinkage. Some further change in the alpha phase and further shrinkage took place during room-temperature aging following the annealing.

4. Prolonged annealing at 95° C. (2 weeks) increased the extent of the aging effects during the subsequent room-temperature aging.

ACKNOWLEDGMENT

The writers appreciate the cooperation of Mr. G. L. Werley in preparing the die-cast specimens, of Mr. J. L. Rodda in performing the microscopic work, and of other members of the Research Division, The New Jersey Zinc Co. Counsel with Mr. E. A. Anderson during the experimental work and in the preparation of the manuscript was especially valuable.

APPENDIX A

RELATIONSHIP OF LATTICE DIMENSION AND COMPOSITION IN ALPHA ALUMINUM-ZINC ALLOYS

For the purpose of determining the relation between the interplanar spacings of the alpha phase and its composition, aluminum-zinc alloys (up to 2.2 per cent Al) were annealed at 375° C., quenched, and examined by the back-reflection method. The annealing was carried out variously from 5 to 23 days, the duration of the annealing beyond 5 days being dependent upon the availability of the X-ray apparatus for examination of the specimens immediately after quenching. Table 4 gives the interplanar spacings of the alpha phase obtained. Two of the several reflections recorded on the X-ray pattern are given in the table, 00.1 (4) and 10.4, which show the highest concentrational sensitivity. The data in Table 4 are given graphically in Fig. 7.

TABLE 4.—*Interplanar Spacings of Alpha Aluminum-zinc Alloys Annealed at 375°C and Quenched*

Total Per Cent Aluminum	Interplanar Spacings	
	00.1 (4)	10.4
0.00	1.2345	1.0881
0.25	1.2383	1.0904
0.40	1.2411	1.0926
0.75	1.2465	
0.95	1.2472	1.0958
2.2	1.2474	1.0960

On the basis of the graphs of Fig. 7 an estimate was made of the aluminum content of the alpha phase in each specimen examined in this

investigation. An average of the estimate for the 10.4 and 00.1 (4) spacings was taken to be the aluminum content of the alpha in question.

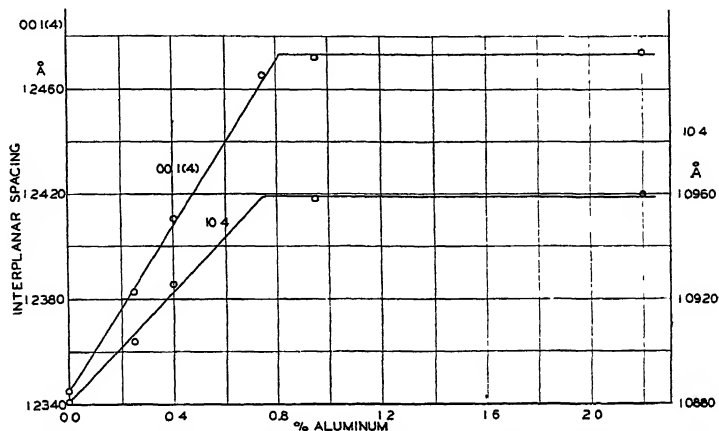


Fig. 7.—A RELATIONSHIP OF LATTICE DIMENSION AND COMPOSITION IN ALPHA ALUMINUM-ZINC.

APPENDIX B

SOLID SOLUBILITY OF ALUMINUM IN ZINC

The solid solubility of aluminum in zinc at 375° C. is indicated by Fig. 7 to be 0.78 per cent. Long aging of the die-casting alloy at room temperature and annealings at various temperatures made possible an estimate of the solid solubility of aluminum in zinc at these temperatures. The aluminum content of the alpha phase, after dimensional stability at a given temperature had been definitely attained, was assumed to be the equilibrium composition at that temperature.

In presenting these data on solubility the authors wish to emphasize that they can be considered only tentative. The inexactness of the data is admitted because of: (1) an insufficient number of annealing temperatures, (2) the alloys not being strictly pure aluminum-zinc alloys and (3) the uncertainty of room-temperature measurements of solid solubility at elevated temperatures. The best

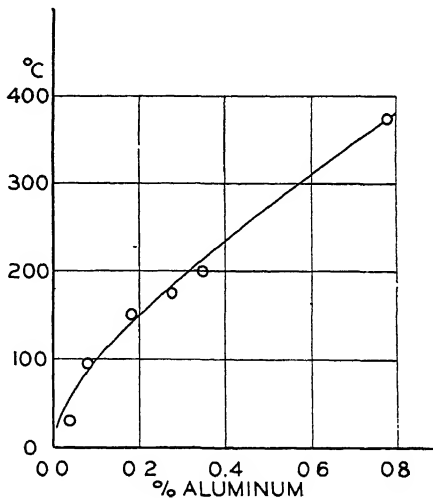


Fig. 8.—SOLID SOLUBILITY OF ALUMINUM IN ZINC.

previous work has been that of W. M. Peirce⁸, of this laboratory, who determined by the electrical conductivity method the solubility at 230° and 335° C. as 0.60 and 0.85 per cent, respectively.

Table 5 gives the experimental values⁹, which are plotted on the solubility curve of Fig. 8.

TABLE 5.—*Measured Values of Solid Solubility of Aluminum in Zinc*

TEMPERATURE, DEG. C.	SOLID SOLUBILITY, PER CENT AL
Room	0.04
95	0.08
150	0.18
175	0.28
200	0.35
375	0.78

⁸ W. M. Peirce: *Trans. A.I.M.E.* (1923) **68**, 767-795.

⁹ The value of 0.18 per cent at 150° C. is an average of the 0.17 per cent indicated by this investigation and 0.19 per cent determined separately in a pure aluminum-zinc alloy.

APPENDIX C

COMPILATION OF X-RAY DATA ON THE ALPHA PHASE

Table 6 gives the measured interplanar spacings of the alpha phase and the lattice values calculated therefrom for the various specimens studied in this investigation.

TABLE 6.—*X-ray Data on Alpha Phase in Zinc-alloy^a Die Casting*

Treatment	Interplanar Spacings				Unit Cell Dimensions		
	00 1 (4)	11.2	10.0 (2)	10.4	a_0	c_0	Axial Ratio, c/a
Room-temperature aging:							
As cast... ..	1.2402	1.1713	1.1509	1.0916	2.6579	4.9602	1.8662
5 wk. room temp....	1.2367	1.1710	1.1510	1.0894	2.6587	4.9465	1.8605
17 wk. room temp ..	1.2348	1.1709	1.1514	1.0890	2.6591	4.9416	1.8584
Post-aging annealing:							
Stabilized at room temp.....	1.2346	1.1706	1.1516	1.0888	2.6593	4.9404	1.8578
14 days 150° C.....	1.2371	1.1710	1.1509	1.0900	2.6585	4.9494	1.8617
27 days 175° C.....	1.2390	1.1712	1.1509	1.0911	2.6579	4.9563	1.8647
Commercial stabilization annealing:							
As cast.....	1.2402	1.1713	1.1509	1.0916	2.6579	4.9602	1.8662
3 hr. 95° C.....	1.2364	1.1709	1.1511	1.0896	2.6584	4.9466	1.8608
5 wk. room temp....	1.2361	1.1709	1.1513	1.0884	2.6593	4.9422	1.8584
19 wk. room temp...	1.2354	1.1711	1.1517	1.0890	2.6597	4.9426	1.8583
Prolonged stabilization annealing:							
As cast.....	1.2402	1.1713	1.1509	1.0916	2.6579	4.9602	1.8662
2 wk. 95° C.....	1.2358	1.1708	1.1513	1.0890	2.6587	4.9436	1.8594
5 wk. room temp..	1.2356	1.1709	1.1514	1.0885	2.6593	4.9415	1.8582
15 wk. room temp...	1.2349	1.1711	1.1516	1.0887	2.6598	4.9406	1.8575

^a A.S.T.M. No. 23 alloy, 4.1 per cent aluminum, 0.04 per cent magnesium, remainder high-purity zinc (99.99+ per cent).

Equilibrium Relations in Aluminum-zinc Alloys of High Purity, II

BY WILLIAM L. FINK*, ASSOCIATE MEMBER A.I.M.E., AND L. A. WILLEY*

(New York Meeting, February, 1936)

SINCE so many different curves have been published for the solid solubility of zinc in aluminum, it seems desirable to definitely establish the correct curve by two or more independent methods. The curve published in part I[†] was based entirely upon X-ray measurements because the other methods employed at that time were not satisfactory. The present paper (the seventeenth of this series on high-purity aluminum alloys) describes the determination of the solid solubility of zinc in aluminum by the measurement of electrical resistivity at temperature and by microscopic examination.

Since the publication of our part I in 1932, an investigation of the solubility relations in the aluminum-zinc system has been reported by Schmid and Wassermann², who obtained their solubility results from lattice-parameter measurements on heat-treated and quenched specimens. The diagram that they published is shown in Fig. 1. In this investigation they also found by X-ray measurements that the parameter of the gamma phase changed continuously with zinc content and at such a rate that it would be identical with that of the beta phase at 60 atomic per cent zinc. It was concluded therefore that the beta and gamma phases, from the point of view of structural relationship, are one single phase. They also suggested a gap of immiscibility between 270° and 350° C. The complete boundary in this region could not be determined satisfactorily by the method employed and therefore was not shown in their diagram.

ALUMINUM-ZINC ALLOYS

Materials Used.—Electrolytically refined aluminum³ was used in preparing the alloys for the work reported in this paper. Chemical analysis showed the following impurities: 0.004 to 0.005 per cent silicon, 0.006 to 0.008 per cent iron and 0.005 to 0.006 per cent copper. Also,

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† References are at the end of the paper.

a zinc of very high purity (triply distilled), obtained from the New Jersey Zinc Co., was used, which showed the following impurities: 0.001 per cent iron, 0.001 per cent aluminum and less than 0.001 per cent each of silicon, copper, lead, cadmium and sodium.

Preparation of Alloys.—The aluminum was melted in a small Hoskins electric crucible furnace. All alloys were prepared by the direct addition of zinc to aluminum at 700° to 750° C. in alundum-lined plumbago crucibles. The alloys were chill-cast in the form of small ingots usually 2 by 9 by 10 cm. or 0.5 by 3.5 by 7.5 cm. The procedure used in rolling the ingots to sheet was varied somewhat, depending upon the alloy. The ingots were given a homogenizing anneal at temperatures ranging from 375° to 525° C. These were furnace-cooled to 250° C., held at that

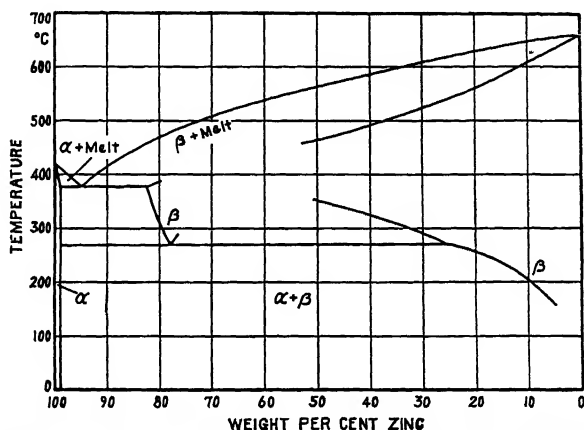


FIG. 1.—DIAGRAM OF ALUMINUM-ZINC SYSTEM (SCHMID AND WASSERMANN).

temperature for 24 hr. and hot-rolled to slabs. The rolled slabs were annealed at 250° C. and cold-rolled to 22-gage (0.064 cm.) or 18-gage (0.102 cm.) sheet. The specimens for resistivity determination at elevated temperatures, and for metallographic examination after heat-treatment and quenching, were cut from the cold-rolled sheet. The specimens for resistivity determinations were 1 cm. by 23 cm. and for metallographic determinations 2 by 2½ cm.

Chemical Analysis.—Portions of the sheet adjacent to the samples used for resistivity and microscopic examination were analyzed for zinc by the zinc mercuric thiocyanate method⁴. The results of the analyses are given in Table 1.

METHODS

The principal method used was measurement of electrical resistivity at elevated temperatures. From these measurements, electrical resistiv-

ity-concentration and electrical resistivity-temperature curves were obtained. The results obtained by this method were checked in part by microscopic examination of heat-treated and quenched specimens.

TABLE 1.—*Chemical Composition of Alloys*

Alloy No.	Chemical Analysis					Alloy No.	Chemical Analysis				
	Weight, Per Cent				Atomic Per Cent Zn		Weight, Per Cent				Atomic Per Cent Zn
	Si	Fe	Cu	Zn			Si	Fe	Cu	Zn	
Y4003	0.005	0.007	0.007	3.00	1.26	S16149	0.004	0.003	0.005	25.3	12.3
Y4004				3.99	1.69	S16150				30.3	15.2
Y4005				4.96	2.11	S16151				35.6	18.6
Y4006				5.96	2.55	S16152				40.6	22.0
Y4007				6.91	2.97	S16153				45.3	25.5
Y4008				7.81	3.38	S16154				50.4	29.6
Y4009				8.98	3.92	S16155				55.6	34.1
Y4010				9.81	4.30	S16156				60.1	38.5
Y4011				10.93	4.82	S18855				64.9	43.3
Y4012				11.70	5.19	S18856				68.0	46.7
Y4013				12.73	5.68	S18857				68.9	47.8
Y4014				13.73	6.17	S18858				69.5	48.5
Y4015				14.83	6.71	S18859				70.9	50.2
Y4016				15.85	7.22	S18860				72.8	52.8
Y4017				16.76	7.67	S18861				74.8	55.1
Y4018				17.63	8.12	S19066				76.8	57.8
Y4019				18.60	8.62	S19067				78.6	60.3
Y4020				0.005	0.007	0.007				19.80	9.25
						S19069			80.4	62.9	
						S19070	0.002	0.002	0.002	81.4	64.4

Apparatus for Electrical Resistivity Determinations.—The electrical resistivities were determined by measuring the potential drop across each specimen and across a standard 0.001-ohm resistance when the same current was flowing through them. The apparatus shown in Fig. 2 was used to hold 12 specimens in the furnace and to make the necessary electrical contacts. The specimen holders ("Alsimag 48" insulating blocks) were mounted on a solid aluminum dodecagonal prism 46 cm. high and 12 cm. between parallel lateral faces. Attached to the insulating blocks were nichrome bars and knife edges furnishing contacts for current and potential leads in addition to holding the specimens securely in position.

The temperature of the specimens was held at any desired value (within one degree Centigrade) in a Leeds & Northrup "Homo" furnace. This close temperature control was made possible by placing the fixture described above inside an aluminum cylinder approximately 50 cm. long by 28 cm. O.D. by 20 cm. I.D. The ends of this cylinder were covered

by aluminum plates to prevent the circulation of air through the cylinder. The large mass of aluminum in the prism and the cylinder effectively prevented the temperature fluctuations in the furnace atmosphere from reaching the specimens.

The apparatus for measuring the potential drop is shown in Fig. 3. The current was furnished by two 6-volt storage batteries not shown in

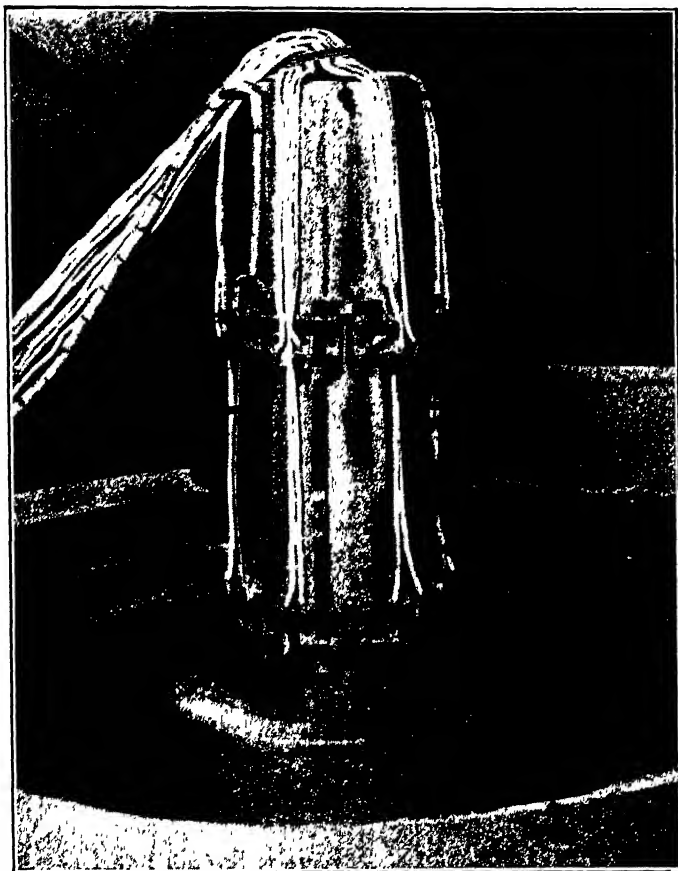


FIG. 2.—APPARATUS FOR HOLDING ELECTRICAL RESISTIVITY SPECIMENS.

the photograph. The current was adjusted by the large slide-wire resistance, which was connected in series with the batteries, the specimens and the standard resistance. The potential drop was measured by the Leeds & Northrup type K potentiometer, which could be connected to the potential leads of any specimen by means of the selector switch.

Heat-treatments for Solid Solubility Determinations.—The method of heat-treating the specimens for obtaining equilibrium was quite important. It has been pointed out in a previous investigation⁶ that the

precipitation of a phase from some aluminum solid solutions was either extremely slow or entirely absent when the alloys were first heated to a homogenizing temperature and then slowly cooled to some temperature below the solubility limit. This was attributed in part to the absence of nuclei in the slowly cooled supersaturated solid solution. It was also found that a much quicker and more complete approach to equilibrium was accomplished by heating homogenized and cold-worked specimens for a relatively long period of time at a low temperature to obtain a very finely divided precipitate, and then heating to the desired temperature.

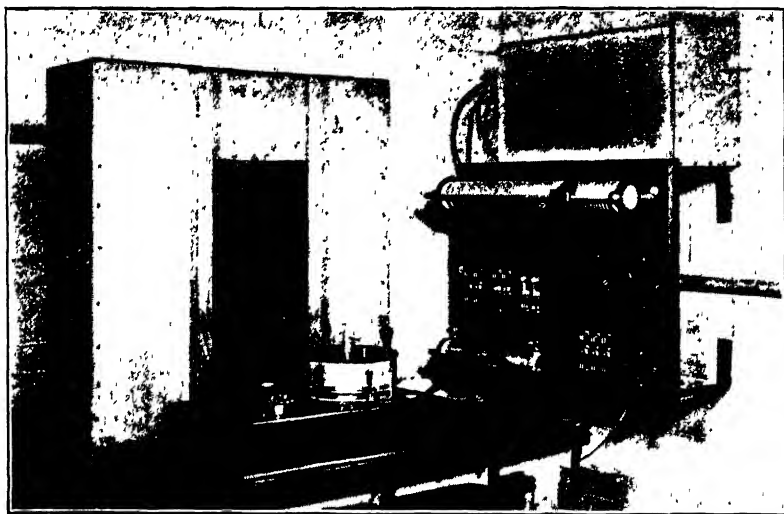


FIG. 3.—APPARATUS FOR MEASURING ELECTRICAL RESISTIVITY OF SPECIMENS.

It was necessary to use this method for producing equilibrium in aluminum-zinc alloy below 275° C. Details of the treatments are listed in Table 2. At all temperatures above 100° C., heating of the specimens was continued until no further significant change in resistivity occurred.

SOLID SOLUBILITY

Solubility of Zinc in Aluminum from 125° to 275° C.—The resistivity-concentration curves obtained from annealed specimens and from cold-worked specimens of alloys containing 1.25 to 9.25 atomic per cent zinc (3 to 20 weight per cent) are shown in Figs. 4 and 5, respectively. These curves show the limits of the solid solubility (i.e., the boundary between the β and $\beta + \alpha$ phase fields) of zinc in aluminum at seven temperatures between 125° and 225° C.

Equilibrium was not attained at 100° C. In the annealed specimens, no indication of precipitation occurred in specimens containing up to

TABLE 2.—*Heat-treatments*

	Temperature, Deg. C.		Time to Reach Temperature, Hr.	Total Time at Temperature, Hr.	Resistivity Measurements, Time after Reaching Temperature, Hr.
	From	To			
Group I ^{a,b}	Room	100	Water quench	5153	
	100	Room			
	Room	100		3	17
	100	125		475	17-144-306-474
	125	150		6	21-70-162-284-497
	150	175		4	1-18-96-164
	175	188		4	1-18-43-91-164
	188	200		3	1-18-42-67
	200	212		4	20-44
	212	225	2	76	45-74
Group II ^a	Room	100	Water quench	721	
	100	Room			
	Room	100		6	15
	100	125		3	44
	125	150		4	213
	150	175		3	65
	175	188		4	92
	188	200		3	73
	200	212		3	91
	212	225	3	73	20-73
Group III ^d	Room	250	9	35	12-34
	250	275	3	19	2-19
	275	288	6	20	1-18
	288	300	2	20	2-20
	300	313	1	48	1-48
	313	325	2	21	3-21
	325	338	3	21	21
	338	350	4	20	3-20
	350	363	1	1	1
	363	387	10	18	17
	387	286	2	67	65
Group IV ^a		285		10	10
	285	291	2	6	6
	291	296	2	14	14
	296	300	2	6	6
	300	309	4	12	12
	309	325	4	20	20
	325	332	2	6	6
	332	340	4	12	12
	340	344	2	6	6
	344	353	4	12	12
	353	359	2	6	6
	359	363	2	14	14
	363	368	2	5	5
	368	Room			
	Room	250		23	4-23

^a All specimens of each group were subjected consecutively to the treatments in the order indicated.

^b Annealed specimens (2 hr. at 300° C., furnace-cooled). Alloys Y4003-Y4004-Y4005-Y4007-Y4009-Y4011-Y4013-Y4015-Y4017-Y4018-Y4019-Y4020.

^c Cold-worked specimens. Alloys Y4003-Y4004-Y4005-Y4007-Y4009-Y4011-Y4013-Y4015-Y4017-Y4018-Y4019-Y4020.

^d Cold-worked specimens. Alloys Y4005-Y4010-Y4015-Y4020 and S16149 to S16156 inclusive.

^e Cold-worked specimens. Alloys S18855 to S18861 inclusive and S19066 to S19070 inclusive.

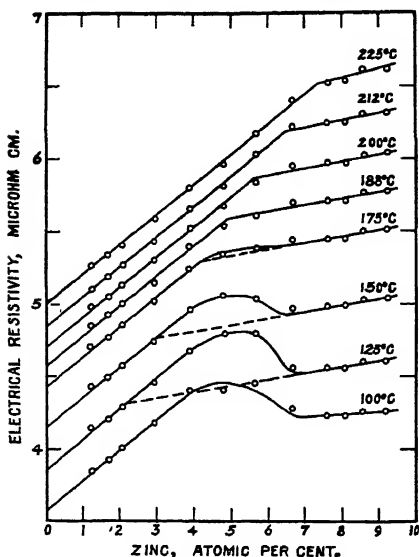


FIG. 4.—ANNEALED SPECIMENS.

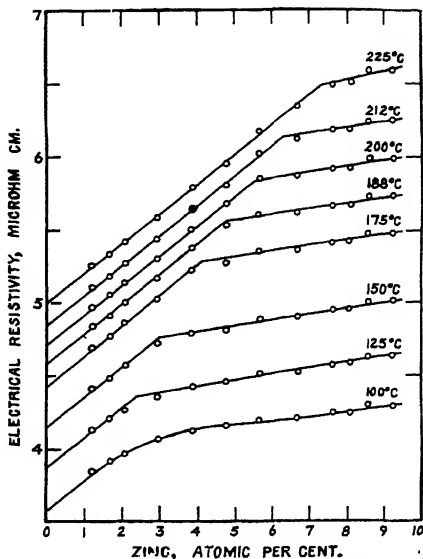


FIG. 5.—COLD-WORKED SPECIMENS.

FIGS. 4 AND 5.—ELECTRICAL RESISTIVITY-CONCENTRATION CURVES FROM SPECIMENS CONTAINING UP TO 9.25 ATOMIC PER CENT ZINC.

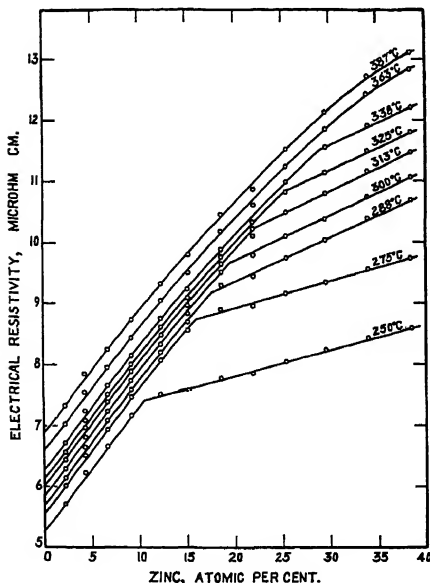


FIG. 6.

FIG. 6.—ELECTRICAL RESISTIVITY CONCENTRATION CURVES FOR SPECIMENS CONTAINING UP TO 38.5 ATOMIC PER CENT ZINC.

FIG. 7.—ALLOY CONTAINING 16.76 WEIGHT PER CENT ZINC (S16425-Y4017-A11951D). $\times 500$.

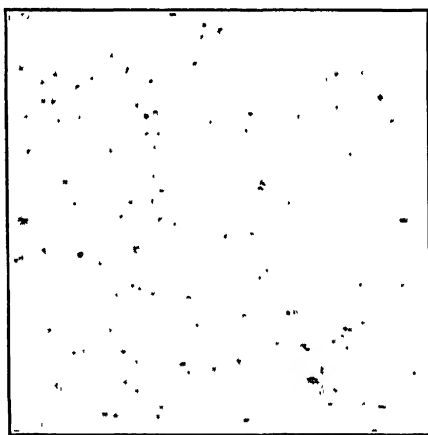


FIG. 7.

Specimen heat-treated 165 hr. at 225° C. and quenched. Shows particles of zinc solid solution in aluminum solid solution matrix. This alloy lies just beyond the solubility limit at 225° C. Etched with 25 per cent HNO_3 at 70° C.

4 atomic per cent zinc in a total of 5173 hr. It was necessary to raise the temperature to 188° C. before all specimens attained equilibrium. However, as equilibrium was attained in specimens containing over 7 atomic per cent zinc at 125° to 175° C., it was possible to extrapolate

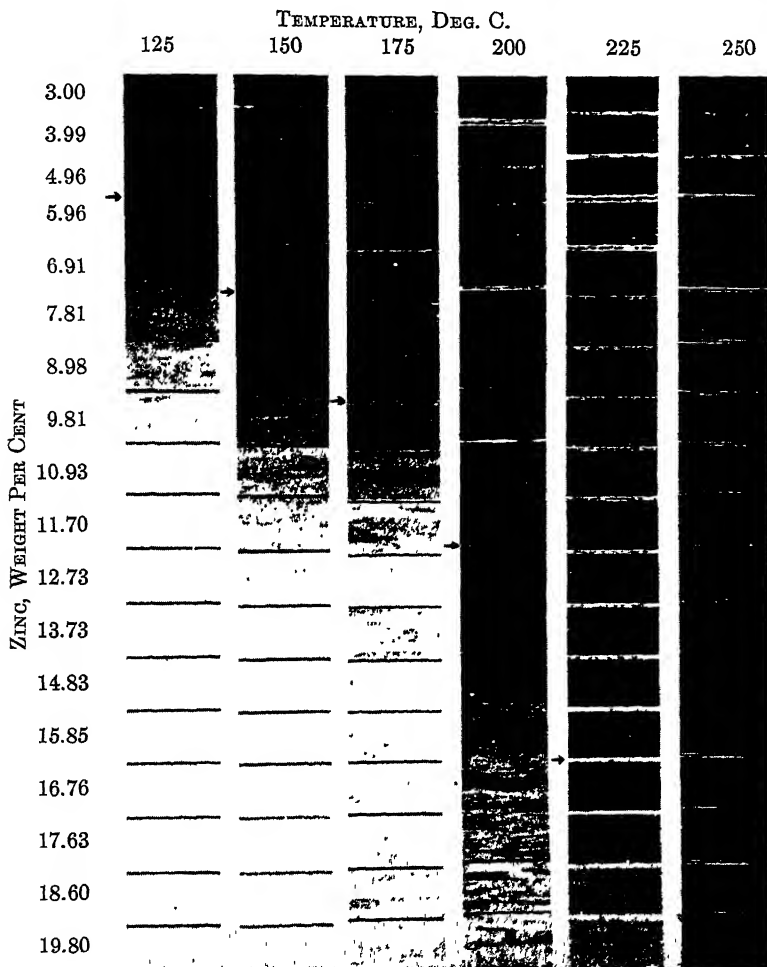


FIG. 8.—COMPOSITE MACROGRAPH. $\times 10$.

Illustrates change in solid solubility with temperature. Arrows show solubility limit. Etched with 25 per cent HNO_3 at 70° C.

the curve from 9.25 to 7.22 atomic per cent until it intersected the other branch of the curve, thus indicating the solid solubility. In all the cold-worked specimens containing more than 1.6 atomic per cent zinc, precipitation occurred at 100° C., although it was not complete after a total of 736 hr. at that temperature. On heating to 125° C. and above, equilibrium was attained.

The electrical resistivity-concentration curves showing the limits of solubility of zinc in aluminum (i.e., the boundary between the β and $\beta + \alpha$ phases) at 250° and 275° C. are shown in Fig. 6.

The microscopic examination of thoroughly heat-treated and quenched specimens gave results that were in agreement with those obtained by electrical resistivity determination. Fig. 7 shows the structure of a specimen containing 16.76 per cent zinc (7.67 atomic per cent) after heat-treating and quenching from 225° C. It shows, in addition to the aluminum solid solution, particles of the zinc solid solution. Even a macroetch will indicate precipitation. A composite macrograph of polished and etched sections of sheet specimens that were heat-treated and quenched from the temperatures indicated is shown in Fig. 8. An examination of these specimens at 10 diameters gives an accurate determination of the solid solubility at different temperatures.

The solubility limits from 125° to 275° C. are given in Table 3.

TABLE 3.—*Solid Solubility of Zinc in Aluminum from 125° to 275° C.*

Temperature, Deg. C.	Saturation Limits					
	From Electrical Resistivity Determinations				From Microscopic Examination	
	Annealed Specimens		Cold-worked Specimens		Cold-worked Specimens	
	Atomic Per Cent Zn	Weight Per Cent Zn	Atomic Per Cent Zn	Weight Per Cent Zn	>Weight Per Cent Zn	<Weight Per Cent Zn
125	2.2	5.2	2.4	5.6	4.96	5.96
150	3.0	7.0	3.0	7.0	6.91	7.81
175	4.2	9.6	4.1	9.4	8.98	9.81
188	4.9	11.1	4.8	10.9		
200	5.7	12.8	5.5	12.4	11.70	12.73
212	6.5	14.4	6.3	14.0		
225	7.4	16.2	7.3	16.0	15.85	16.76
250			10.6	22.3	19.80	
275			16.0	31.6		

Solid Solubility of Zinc in Aluminum from 275° to 350° C.—A discontinuity in the zinc-solubility curve (i.e., the boundary between the β and $\beta + \alpha$ phase fields) occurs at 275° C. At this temperature the solubility of zinc suddenly increases from 31.6 per cent zinc by weight (16 atomic per cent) to 77.7 per cent zinc by weight (59.0 atomic per cent). From 275° to 350° C. the solubility increases rather slowly with the temperature, as shown by the resistivity-temperature curves of Fig. 9 and the values of Table 4. An extrapolation of this branch of the curve shows a solubility of 83.0 weight per cent zinc at 380° C. These results are in substantial agreement with those of several investigators⁷.

TABLE 4.—*Solid Solubility of Zinc in Aluminum from 275° to 350° C.*

Temperature, Deg. C.	293	312	330	350
Saturation limit: weight per cent zinc.....	78.6	79.5	80.4	81.4
atomic per cent zinc . . .	60.3	61.6	62.9	64.4

Solubility Gap.—In the region from 31.6 per cent to 77.7 weight per cent zinc at temperatures just above 275° C. there is a solubility gap. Two aluminum solid solutions (β_1 and β_2) are in equilibrium in this phase field. As the temperature increases the compositions of these phases approach each other and coincide at 353° C.

The boundary of this solubility gap as determined by electrical resistivity measurements is shown by the resistivity-concentration curves in Fig. 6 and the resistivity-temperature curves in Fig. 10. The results are summarized in Table 5.

A microscopic examination of specimens in the range from 35.6 to 81.4 weight per cent zinc after heat-treatments at 335° and 365° C. for 23 hr. and a cold-water quench confirmed the results obtained by the electrical resistivity determinations. The structure of alloys containing between approximately 50 and 70 per cent zinc by weight indicated that a duplex structure had existed at 335° C. Micrographs illustrating the structures of these alloys are shown in Figs. 11 to 16. The darker areas are the decomposition products of the unstable aluminum solid solution (β_2) that existed at 335° C., while the white areas represent the aluminum solid solution (β_1) containing considerably less zinc. After quenching from 365° C. and aging at room temperature for a short time, the structure of all samples in this range indicated that previous to quenching a homogeneous solid solution (β) had existed at that temperature. Representative structures of the alloys quenched from 365° C. are shown in Figs. 17 and 18.

Check on Attainment of Equilibrium.—The results given in Tables 3 and 5 were all obtained by heating specimens to successively higher

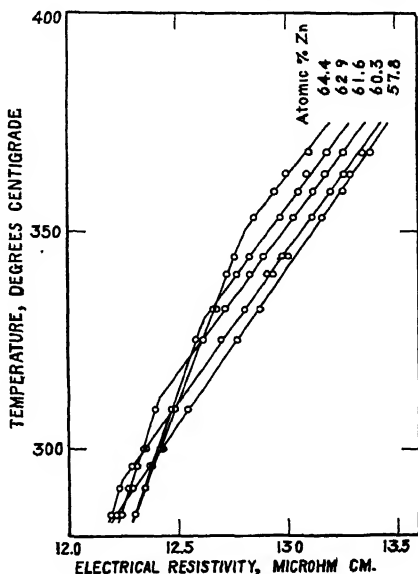


FIG. 9.—ELECTRICAL RESISTIVITY-TEMPERATURE CURVES FOR SAMPLE JUST ABOVE THE EUTECTOID COMPOSITION.

TABLE 5.—*Solubility Gap in Aluminum-zinc System*

Temperature, Deg. C	Aluminum Solid Solution (β_1)		Aluminum Solid Solution (β_2)	
	Atomic Per Cent Zn	Weight Per Cent Zn	Atomic Per Cent Zn	Weight Per Cent Zn
275 ^a	16.0	31.6		
288 ^a	17.6	34.1		
300 ^a	19.6	37.1		
306			55.1	74.8
311	22.0	40.6		
313 ^a	22.2	40.9		
324			52.8	72.8
325 ^a	25.2	44.9		
327	25.5	45.3		
335			50.2	70.9
338 ^a	28.8	49.5		
340	29.6	50.4		
341			48.5	69.5
342			47.8	68.9
346			46.7	68.0
350	34.1	55.6		
351			43.3	64.9
353	38.5	60.1	38.5	60.1

^a From electrical resistivity-concentration curves. All other values from electrical resistivity-temperature curves.

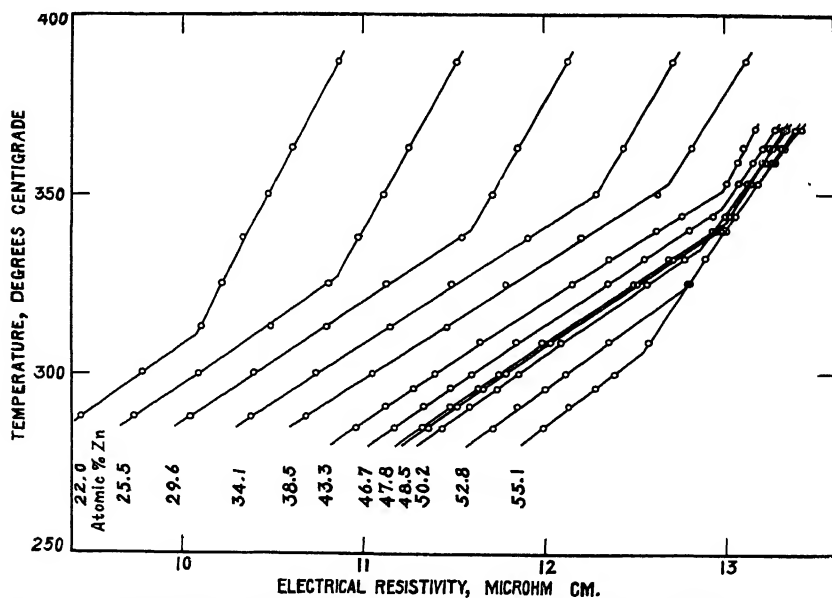
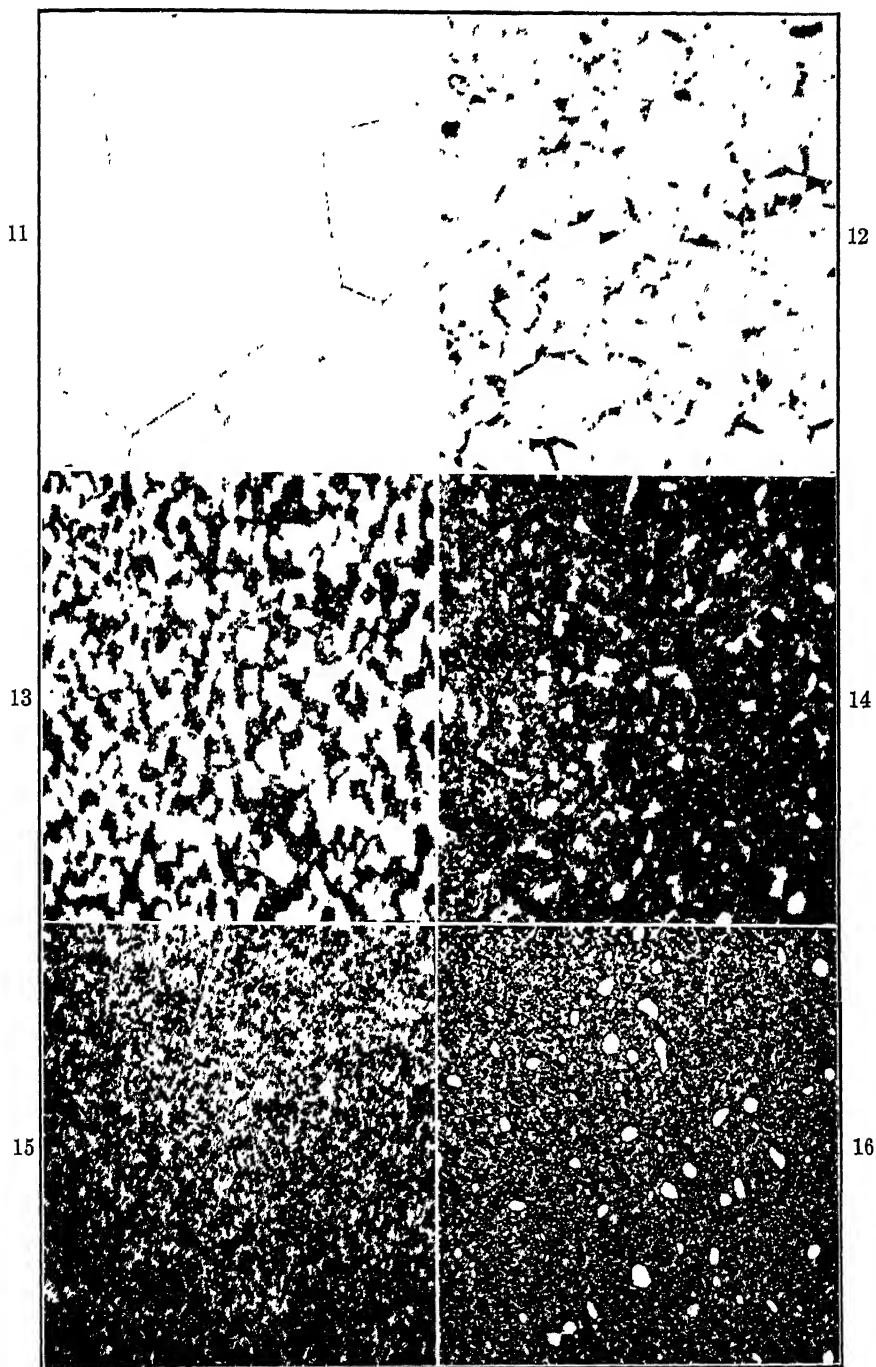


FIG. 10.—ELECTRICAL RESISTIVITY-TEMPERATURE CURVES FOR SPECIMENS IN REGION OF SOLUBILITY GAP.



FIGS. 11-16.—CAPTIONS ON PAGE 256.

temperatures and holding at each of the temperatures until no significant change in resistivity occurred. To determine how nearly equilibrium conditions were attained by that method two determinations were made in which the specimens were cooled from higher temperatures and held

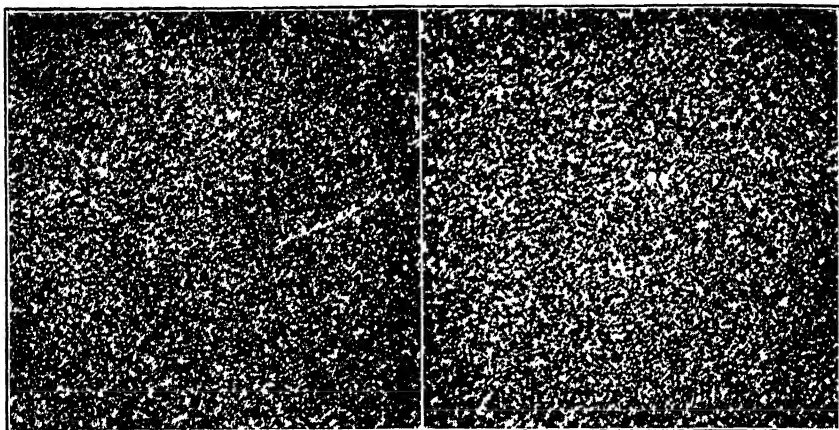


FIG. 17.

FIG. 18.

FIG. 17.—ALLOY CONTAINING 60.1 WEIGHT PER CENT ZINC (S20787-1-S16156-A11974D) $\times 500$.

Specimen heat-treated 23 hr. at 365° C. and quenched. Shows uniformly decomposed structure indicating that a homogeneous solid solution β had existed at 365° C. Etched with 25 per cent HNO_3 .

FIG. 18.—ALLOY CONTAINING 69.5 WEIGHT PER CENT ZINC (S20787-2-S18858-A11942D). $\times 500$.

Specimen heat-treated 23 hr. at 365° C. and quenched. Shows uniformly decomposed structure similar to that of Fig. 17. Etched with 25 per cent HNO_3 .

FIG. 11.—ALLOY CONTAINING 45.3 WEIGHT PER CENT ZINC (S20786-1-S16153-A11959D). Specimen heat-treated 23 hr. at 335° C. and quenched. Shows a single phase structure. Etched with 25 per cent HNO_3 .

FIG. 12.—ALLOY CONTAINING 50.4 WEIGHT PER CENT ZINC (S20786-1-S16154-A11960D). Specimen heat-treated 23 hr. at 335° C. and quenched. Shows areas of decomposed β_2 solid solution in the more stable β_1 matrix. Etched with 25 per cent HNO_3 .

FIG. 13.—ALLOY CONTAINING 60.1 WEIGHT PER CENT ZINC (S20786-1-S16156-A11944D). Specimen heat-treated 23 hr. at 335° C. and quenched. Shows nearly equal amounts of β_1 (white areas) and decomposed β_2 (dark areas). Etched with 25 per cent HNO_3 .

FIG. 14.—ALLOY CONTAINING 69.5 WEIGHT PER CENT ZINC (S20786-2-S18858-A11937D). Specimen heat-treated 23 hr. at 335° C. and quenched. Shows a small amount of β_1 in the matrix of decomposed β_2 . Etched with 25 per cent HNO_3 .

FIG. 15.—ALLOY CONTAINING 72.8 WEIGHT PER CENT ZINC (S20786-2-S18860-A11938D). Specimen heat-treated 23 hr. at 335° C. and quenched. Shows completely decomposed structure indicating that a homogeneous solid solution β had existed at the heat-treating temperature. Etched with 25 per cent HNO_3 .

FIG. 16.—ALLOY CONTAINING 81.4 WEIGHT PER CENT ZINC (S20786-2-S19070-A11985D). Specimen heat-treated 23 hr. at 335° C. and quenched. Shows zinc solid solution particles in a decomposed β matrix. Etched with 0.5 per cent HNO_3 . All $\times 500$.

at a given temperature until the resistivity became substantially constant. The resistivity-concentration curves in Fig. 19 show the comparison; H-288° C. is the curve obtained on heating to 288° C. and C-286° C. that obtained on cooling to 286° C.

The differences between these two curves are largely accounted for by the difference in temperature (2° C.). Calculations indicate that the total deviation from equilibrium did not exceed more than a few hundredths of an atomic per cent of zinc.

The resistivity-composition curves obtained by heating to 275° C. (H-275° C.) and by cooling to 275° C. (C-275° C.) differed considerably

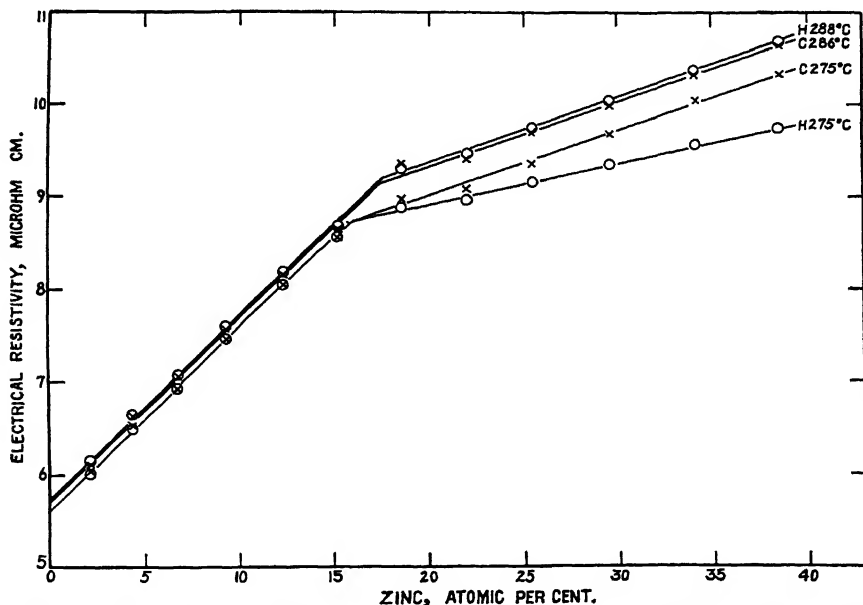


FIG. 19.—ELECTRICAL RESISTIVITY-CONCENTRATION CURVES OBTAINED BY HEATING AND COOLING, AS A CHECK ON ATTAINMENT OF EQUILIBRIUM.

above the solid solubility limit, although both curves gave the same value for the solid solubility (16 atomic per cent). The differences in the slope of the outer branches of the curve is a result of the eutectoid transformation. The curve H-275° C. gives the resistivity of alloys in which aluminum solid solution is in equilibrium with zinc solid solution. The curve C-275° C. gives the electrical resistivity of specimens in which two aluminum solid solutions are in equilibrium.

Eutectoid Transformation.—The intersections of the immiscibility loop with the solid solubility curves indicate that 275° C. is the eutectoid temperature. Moreover, the resistivity-composition curves at 275° C., described above, indicate that 275° C. is very near the eutectoid tem-

perature. In order to determine this temperature more directly, resistivity-temperature curves on heating through the transformation range were obtained for 12 alloys. Resistivity curves for five alloys were also run both on heating and cooling, using a heating rate of approximately $15^{\circ}\text{C. in 24 hr.}$ and a cooling rate of 1° in 24 hr. from 283° to 255°C. The eutectoid temperature as given by the heating curves was

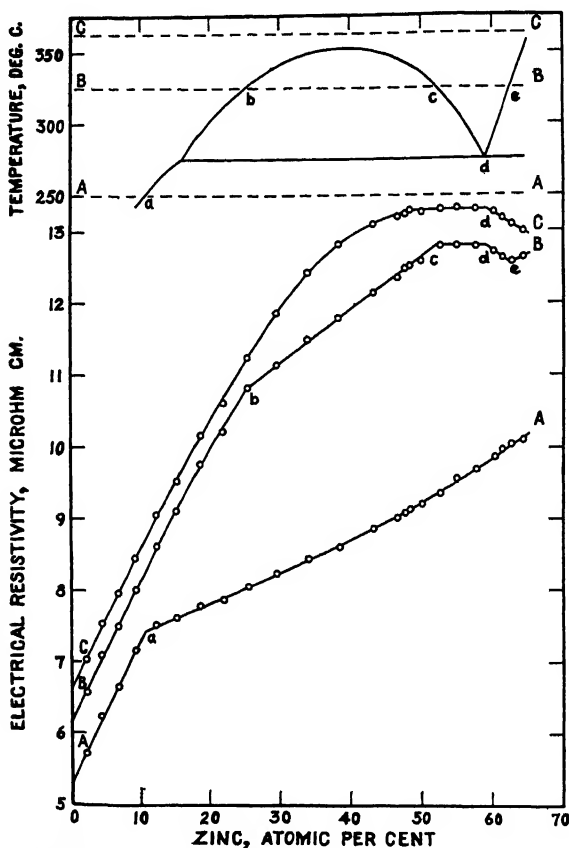


FIG. 20.—TYPICAL ELECTRICAL RESISTIVITY-CONCENTRATION CURVES IN COMPARISON WITH THE EQUILIBRIUM DIAGRAM.

276°C. and as given by the cooling curves was 272°C. These values are reasonably consistent with the temperature 275°C. , which was determined as described above. The value of 275°C. has previously been reported by Ishihara³.

DISCUSSION OF RESULTS

The results of this investigation are well illustrated by the typical curves given in Fig. 20. The breaks in the isothermal electrical resistivity

curves clearly indicate the phase boundaries in the temperature-composition diagram. There is one feature of the curves that has not been explained. All of the resistivity curves taken at temperatures above the eutectoid transformation exhibit a break at the eutectoid composition. Inasmuch as this examination was limited to a study of the solid solubility of zinc in aluminum, the significance of this break in the resistivity curves has not been further investigated. It is, however, of interest to note that this composition approximates that of the possible compound Al_2Zn_3 , which other investigators have suggested.

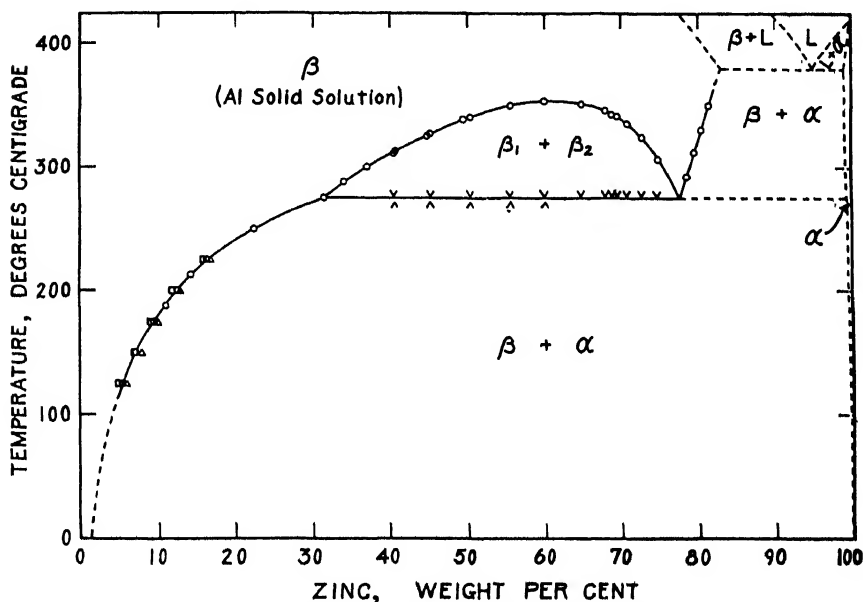


FIG. 21.—EQUILIBRIUM RELATION IN THE ALUMINUM-ZINC SYSTEM.

- From electrical resistivity determinations.
- From microscopic examination, aluminum solid solution.
- △ From microscopic examination, aluminum solid solution plus zinc solid solution.
- ∨ From electrical resistivity-temperature curves, on heating.
- ∧ From electrical resistivity-temperature curves, on cooling.

It will be noted that the values given in the first part of this paper for the solubility of zinc at 200° and 250° C. are too low. It was found in recent experiments that this was caused principally by extended room-temperature precipitation after homogenizing and before powdering. It is believed that the preferential grain-boundary precipitation, which is known to have occurred during the room-temperature aging of the solid specimen, produced heterogeneous powder—i.e., some particles contained more zinc than others. This composition variation was not eliminated by annealing the powder because there was no appreciable diffusion from particle to particle.

ALUMINUM-ZINC SOLID SOLUBILITY CURVE

Fig. 21 shows the solid solubility curve in weight per cent. The solubility increases from 5.4 per cent at 125° C. to 31.6 weight per cent zinc at 275° C., then suddenly increases to 77.7 per cent and slowly increases to 81.4 per cent at 350° C. A solubility gap in the aluminum solid solution extends from 31.6 to 77.7 weight per cent zinc just above 275° C. At higher temperatures, the solubility gap narrows and finally disappears at 353° C. and 60 per cent.

ACKNOWLEDGMENT

The authors desire to express appreciation to Mr. H. V. Churchill, under whose direction the chemical analyses were made, and to Mr. C. J. Walton, who performed some of the metallographic work.

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2. E. Schmid and G. Wassermann: Über das System Aluminum-zinc. *Ztsch. Metallkunde* (1934) **26**, 145.
3. F. C. Frary: Electrolytic Refining of Aluminum. *Trans. Amer. Electrochem. Soc.* (1925) **47**, 275.
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5. American Lava Corporation, Chattanooga, Tennessee.
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7. See reference 1 above (part I of this paper) for list of references.
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DISCUSSION

(E. H. Dix, Jr. presiding)

E. H. DIX, JR.,* New Kensington, Pa.—The session this morning is on aluminum. It was so arranged to commemorate the fiftieth anniversary of the discovery by Charles Martin Hall of the present commercial process for electrolytically producing aluminum. As we try to appreciate what has happened in the aluminum industry in the past 50 years, we realize that it has been a crowded period. Coming just a little bit closer to home, the period of existence of the Aluminum Research Laboratories, established by Dr. Frary about 1919, represents about one-third of that 50 years and during perhaps one-fourth of this 50-year period these laboratories have been working particularly on equilibrium relations in aluminum alloys.

At first, we were interested primarily in the solid solubility because there lay the possibility of heat-treatable alloys. The early work was relatively simple. The paper now under discussion, by W. L. Fink and L. A. Willey, is the seventeenth of this series and in getting into the aluminum-zinc system, particularly the aluminum end, the work has been far from simple.

* Metallurgist, Aluminum Research Laboratories,

E. A. ANDERSON,* G. EDMUNDS* AND M. L. FULLER,* Palmerton, Pa. (written discussion).—This paper represents a distinct contribution to the existing literature on the zinc-aluminum equilibrium diagram. From their data, the authors have constructed the central portion of the diagram to show the fields formerly called beta and gamma to be continuous with a zone of immiscibility existing below about 360° C. This concept of a continuous gamma solid solution must be scrutinized with great care, because its acceptance requires the denial of the existence of the peritectic reaction at 443° C. noted by several of the earlier workers on the system. Schmid and

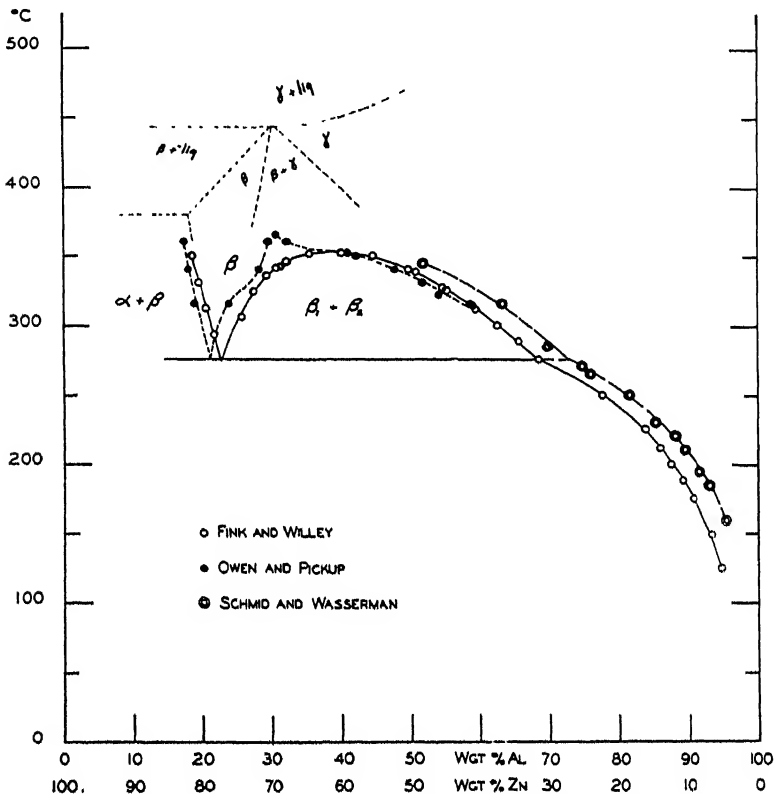


FIG. 22. DATA OF FINK AND WILLEY, OWEN AND PICKUP, AND SCHMID AND WASSERMAN.

Wasserman⁹, who earlier suggested this concept, were distinctly unwilling to choose between the two alternatives on the basis of the data then available.

The data in the present paper are in excellent general agreement with those of Schmid and Wasserman and with the more recent work of Owen and Pickup¹⁰. In Fig. 22, we have plotted these three sets of data. The shape of the upper portion of the diagram as developed by Hanson and Gayler¹¹ is indicated by dotted lines. While

* Research Division, New Jersey Zinc Co., Palmerton, Pa.

⁹ Reference 2.

¹⁰ E. A. Owen and L. Pickup: *Phil. Mag.* (1935) [7] 20, 761.

¹¹ D. Hanson and M. L. V. Gayler: *Jnl. Inst. Met.* (1922) 27, 267.

the Fink and Willey data indicate a smooth immiscibility loop, Owen and Pickup find three points somewhat above the path of the smooth curve, which strongly indicate the existence of a narrow two-phase field between the beta field and the gamma solid solution in agreement with the work of Tanabe¹². Such a field, of course, would be required if a peritectic reaction occurs.

Rosenhain and Archbutt¹³, Bauer and Vogel¹⁴ and Ishihara¹⁵ have presented evidence indicating the existence of a peritectic reaction involving a very small evolution of heat. While doubt may be cast upon the validity of these findings because of the relatively low purity of the metals used, it is significant that no data obtained by direct experiment in the region in question have been presented to disprove the existence of a peritectic.

We believe that while the present paper represents a distinct contribution to the subject, the ultimate answer to the question of the exact nature of the central portion of the diagram cannot be obtained from the existing data. A careful investigation, with pure alloys, of the peritectic horizontal and of the solidus curve seems to be required if the question of the existence of a peritectic is to be answered. If such an investigation failed to reveal a peritectic horizontal, further tests with alloys of known impurity content would seem to be justified in order to explain the halt detected by the earlier workers.

It is unfortunate that the authors were unable to study further the break shown at *d* in the resistivity-concentration curves in Fig. 20. The occurrence of such a break in a supposedly homogeneous field would seem to be indicative of some previously undetected discontinuity.

It would be interesting to learn whether the specimens represented in Figs. 11 to 18, inclusive, were subjected to complete metallographic polishing after quenching or were suitably prepared before annealing so as to require only a light repolishing and etching. Variations in the degree of surface working might account for the fact that the 45.3 per cent zinc alloy shows a homogeneous structure while the other alloys in the series, all quenched from the same homogeneous field, show a duplex structure. This difference in microstructure within an alleged homogeneous field warrants discussion by the authors.

The aluminum content of 0.001 per cent found in the pure zinc used by the authors is somewhat surprising. Metal of this grade will normally contain less than 0.0001 per cent of aluminum.

M. L. V. GAYLER, * Teddington, Middlesex, England (written discussion).—The authors' results, and their interpretation of them, are exceedingly interesting, particularly in view of Owen and Pickup's results¹⁶, which the present authors apparently had not seen. Substantially both investigations lead to about the same conclusion; Fink and Willey, however, consider that there is a solubility gap in which two aluminum solid solutions $\beta_1 + \beta_2$ are in equilibrium, while Owen and Pickup, as a result of their X-ray analysis, remark, "The present X-ray data do not confirm the existence of the ($\beta + \gamma$) region above about 360° C., but, if it exists, it covers a range of composition much less than 1 per cent." From their data, it appears that such a gap must lie between about 69 and 70 per cent zinc, and the present experimental data, obtained from alloys of composition 68, 68.9, 69.5, 70.9 and 72.8 per cent zinc, overlap

¹² T. Tanabe: *Jnl. Inst. Met.* (1924) **32**, 415-453.

¹³ W. Rosenhain and S. L. Archbutt: *Trans. Roy. Soc.* (1912) **211A**, 315.

¹⁴ O. Bauer and O. Vogel: *Int. Ztsch. Metallographie* (1916) **8**, 101.

¹⁵ Reference 8.

* The National Physical Laboratory.

¹⁶ Reference of footnote 10.

this gap. The results of these investigations supplement each other and, together with the further microscopical evidence put forward by Fink and Willey, indicate the existence of the solubility gap as suggested by the latter.

The complete diagram as it stands needs adjustment, which, however, cannot be made easily. Fig. 23 represents a theoretical diagram based on the above facts. The question arises, however, what happens to the peritectic reaction at 443°C. if such a

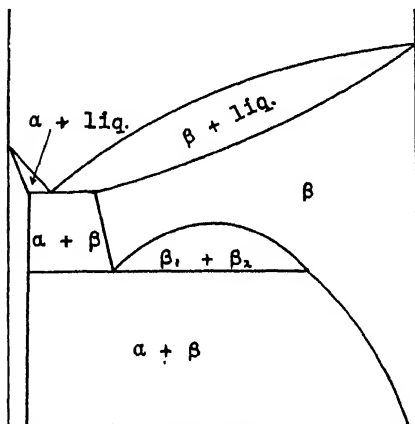


FIG. 23.

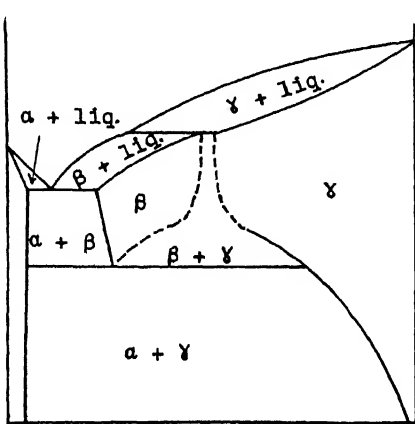


FIG. 24.

diagram holds? There is a possibility that this reaction might not exist in a series of alloys made with zinc and aluminum of the highest purity. The writer, therefore, has made up such a series using French aluminum of high purity, of the following chemical analysis: Fe, 0.001 per cent; Si, 0.005; Cu, 0.001; Ti, trace. The zinc used was spectroscopically pure. Thermal curves showed, both on heating and cooling, that some reaction must take place at about that temperature.

Since a horizontal line appears to exist in the equilibrium diagram, the type diagram must be either that of Fig. 24, as suggested from Tanabe's and Owen and Pickup's results, which, however, the present experimental data do not support, or else a diagram like that given in Fig. 25. In the latter, a region of liquid immiscibility exists, and this would eliminate the existence of a β phase, as distinct from the γ phase: but the existence of such a region in the aluminum-zinc system is highly improbable. On the other hand, the possibility arises that the thermal transformation taking place at about 443°C. is not a phase change at all, and as such has no existence in an equilibrium diagram. If this were so, Fig. 23 would represent the facts obtained.

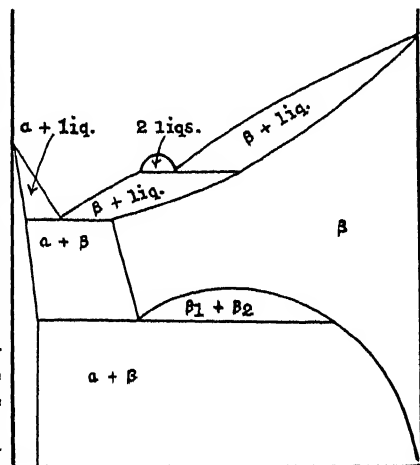


FIG. 25.

The writer is carrying out experiments to check this point, but the results cannot be obtained in time to communicate them now. It is hoped that they will be published shortly.

W. L. FINK AND L. A. WILLEY (written discussion).—The statement in the discussion by Messrs. Anderson, Edmunds and Fuller, "This concept of a continuous gamma solid solution must be scrutinized with great care since its acceptance requires the denial of the existence of the peritectic reaction at 443° C. noted by several of the earlier workers on the system," is answered by Dr. Gayler's discussion and the authors' reply thereto (below). Messrs. Anderson, Edmunds and Fuller evidently misunderstood the authors' statements concerning Figs. 11 to 18. The specimen containing 45.3 weight per cent zinc was quenched from a homogeneous field and after quenching no significant decomposition had occurred prior to the polishing. The slow rate of

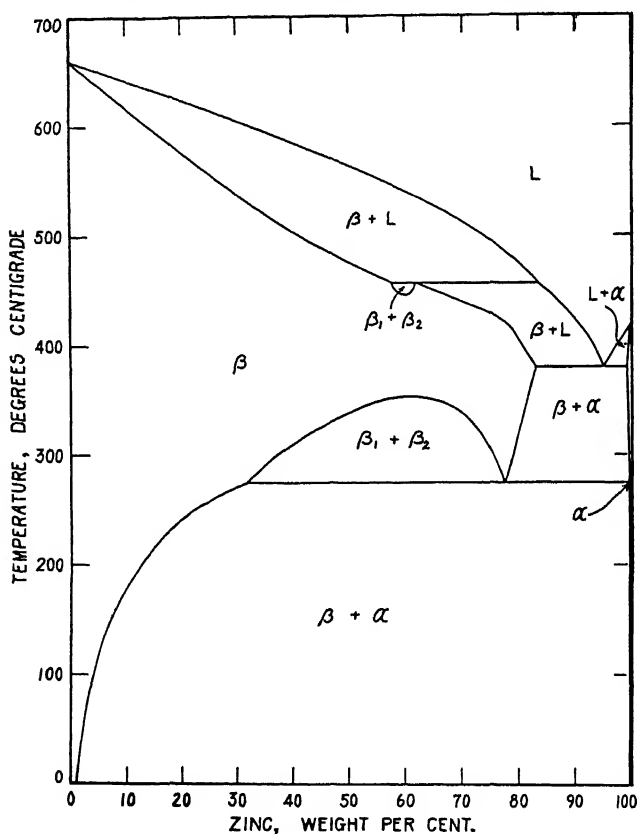


Fig. 26.

decomposition of the β_1 phase into α and β is characteristic of the solid solutions containing less than about 60 weight per cent zinc, the rate decreasing with decreasing zinc content. The β_2 phase and β solutions that contain more than approximately 60 weight per cent zinc decompose rapidly. It is this difference in rate of decomposition that permits microscopic identification of the phases β_1 and β_2 . Figs. 12, 13 and 14 show the structures of alloys containing 50.4, 60.1 and 69.5 weight per cent zinc after they were quenched from within the two-phase field. The light areas are the β_1 phase, whereas the darker areas resembling troostite are the decomposition products of the β_2 phase. Figs. 15, 17 and 18 represent alloys quenched from a homogeneous field. The alloys contained 72.8, 60.1 and 69.5 weight per cent respectively, so that

decomposition was rapid. The microstructure therefore consists entirely of the troostitic decomposition products, showing that the samples originally consisted entirely of one phase (β). Fig. 16 shows the structure of an alloy containing 81.4 weight per cent zinc. This alloy was quenched from the two-phase field, β and α . The white areas are the α phase, and the matrix is the decomposition product from the β phase which existed at the heat-treating temperature.

It is interesting to learn that Dr. Gayler has confirmed the existence of the peritectic in this system even when the alloys are prepared from metals of very high purity. In her discussion it is pointed out that the existence of the peritectic reaction and the immiscibility loop β_1 and β_2 are not incompatible. In Figs. 1 to 3 are listed possible types of diagrams for this system. Dr. Gayler overlooked one possibility, the one that the authors consider most probable. This possibility is shown in Fig. 26. The authors have located the points by making the best guesses from the data available and have drawn the diagram to scale. This diagram is not only consistent with the peritectic reaction and the immiscibility loop β_1 and β_2 , but offers an explanation for previous results obtained with low-purity alloys. It would not be surprising if the presence of other alloying elements should enlarge the two β_1 - β_2 fields until they merged. This would give the type of diagram previously reported by Dr. Gayler and other workers.

Density Changes in Solid Aluminum Alloys

By L. W. KEMPF,* MEMBER A.I.M.E., AND H. L. HOPKINS*

(New York Meeting, February, 1936)

ALUMINUM alloys, in common with most other metallic alloys exhibit slight density changes with variations in temper achieved by heat-treatment, which usually are the result of the variation with temperature of the solid solubility of the various alloy constituents in the solvent metal. Changes in density are, of course, most marked in conditions that exhibit the maximum variation in solid solubility of the constituents. In aluminum alloys these conditions usually prevail when alloys are quenched from just below the melting point and are subsequently reheated to some lower temperature. Since commercial heat-treatments may be of this type, the density changes, although small (of the order of 0.3 per cent which may be compared with the density change of about 1.5 per cent involved in the transformation, at ordinary temperatures, of gamma to alpha iron during the hardening of steel), may in some specific applications necessitate quantitative consideration. This phenomenon has been investigated extensively in the laboratories of the Aluminum Company of America over a period of years.

A number of investigators^{1-5†} have observed and measured the density changes accompanying the heat-treatment of aluminum alloys. In general, these changes have not been directly translated to dimensional changes and their significance has been overlooked to some extent by the practical user of aluminum alloys. It is the purpose of this paper to consider some practical aspects of these density and dimensional changes.

These density changes were given some consideration in 1917 in connection with the use of aluminum-alloy pistons for aircraft engines. Investigations by Lea and Shakespear were reported in some confidential reports of the British Advisory Committee for Aeronautics, Light Alloys Subcommittee, during 1917 and 1918, which are not generally available in published form. In these reports the term "permanent growth" was applied to the dimensional changes occurring in the pistons at the tem-

Manuscript received at the office of the Institute Dec. 2, 1935.

* Aluminum Research Laboratories, Aluminum Company of America, Cleveland, Ohio.

† References are at the end of the paper.

perature of operation and persisting on cooling to ordinary temperatures. This terminology was probably the result of an attempt to differentiate between permanent dimensional changes and the temporary changes due to the normal thermal expansion of the metal. In usage, the term is frequently shortened to "growth," and in this sense it will be used in this paper. Lea and Shakespear found that some copper-containing alloys of undetermined structural condition showed unit linear growths of about 0.0006 to 0.0008; also, that in these aluminum-copper alloys complete growth could be brought about by heating in the temperature range 340° to 360° C. (644° to 680° F.). It was concluded that the permanent growth of the alloys investigated was so small as compared with the thermal expansion at the supposed operating temperatures that it was not worth practical consideration.

Considerable effort was devoted to the study of the growth of 122 alloy in the laboratories of the Aluminum Castings Co. in 1919 by E. H. Dix, Jr., and somewhat later (1920) by A. E. Becker. They came to the conclusion that complete growth could be produced by heating this alloy for a short period of time at temperatures in the neighborhood of 260° C. (500° F.) and higher. The practical application of heat-treatments involving temperatures in this range resulted in relatively low hardness. Because of this and the ensuing development of pistons in which growth was not supposed to be objectionable, the treatment was soon abandoned.

In 1927, as the result of some observed phenomena in specialized applications of aluminum-alloy automotive pistons, R. S. Archer and W. L. Pink, in these laboratories, made a careful investigation of the growth of 122 alloy, especially in temperature ranges lower than those used by previous investigators. They demonstrated that the time to maximum growth was a logarithmic function of temperature. It appeared fairly obvious that growth must be associated in some manner with decomposition of supersaturated solid solutions. Small dimensional changes are important in a few applications other than pistons, and it became desirable to determine the amount and rate of growth accompanying changes in structure in the common aluminum alloys.

EXPERIMENTAL PROCEDURE FOR DETERMINING GROWTH

A number of methods are available and have been used for the determination of permanent growth. The two fundamental methods are: (1) accurate determination of changes in density, and (2) precise determination of changes in linear dimension. The first method has been used in a number of instances by other investigators but the results have not generally been translated to dimensional changes. In the use of this method, it is almost imperative that wrought specimens be used, because of the nonuniform distribution of porosity in most castings. Where

wrought specimens can be used, this method is probably inherently the most accurate, inasmuch as density measurements can be readily made with an accuracy of about one part in 10,000. The second method has the advantage of being a direct determination of the quantity of most practical interest. It also has the advantage of utilizing relatively large specimens in which a minor amount of porosity is unimportant. It has as a disadvantage the difficulty of obtaining the requisite degree of precision with ordinary means of measurement.

It has been found⁶ that the measurement of cylinders 5 in. in diameter, with good micrometers reading to 0.0001 in., taking obvious precautions to keep temperature changes within $\pm 0.5^\circ$ C. and averaging a relatively large number of readings, yields measurements accurate to about ± 0.00003 in. per inch. With a unit growth of 0.001 this gives a maximum error of ± 3 per cent for one determination, and since growth is the difference between two such series of measurements, the error in a single determination might be as large as ± 6 per cent. When it is considered, however, that with a specific set of conditions growth proceeds gradually to a definite maximum, it will be recognized that the maximum growth can be determined with a probable error much lower than indicated above for a single determination. Some determinations have also been made on cylindrical bars about 8 by 2 in. in diameter, determining the length changes with an end comparator reading to 0.0001 cm. The results with the end comparator do not appear to be sufficiently more accurate than the micrometer to justify the much greater time necessary. Measurements by all methods have been used in these laboratories with satisfactorily comparable results, and the values obtained for similar alloys and conditions agree well with those appearing in the literature. For example, we have found, using the micrometer and end-comparator methods, that the maximum unit linear growth of an aluminum-copper alloy containing about 6 per cent copper quenched from 538° C. (1000° F.) and reheated to 225° C. (436° F.) is 0.00151. Similarly, Kokubo and Honda⁴ have found by density measurements on approximately the same alloy in the same condition a density that corresponds to a unit linear change of 0.00153. The density changes of other investigators when reduced to unit linear changes agree well with our measurements. It goes without saying that the temperature of measurement must be determined accurately and all measurements reduced to a common temperature.

EXPERIMENTAL RESULTS

If growth is the result of precipitation from, or decomposition of, solid solutions, it should vary with temperature of reheating in much the same manner as the solubility of the element concerned in solid aluminum. Table 1 gives the unit linear changes exhibited on reheating a 6 per cent

copper alloy to various temperatures from 225° (436°) to 500° C. (932° F.) following quenching from an extended solution treatment at 538° C. (1000° F.). The specimens were reheated at the temperatures indicated

TABLE 1.—*Effect of Temperature of Reheating on Amount of Total Growth*
CHILL-CAST 6.08 PER CENT CU (0.03 PER CENT FE, 0.09 PER CENT SI) ALLOY
QUENCHED FROM 15 HR. AT 538° C. (1000° F.)

Temperature of Reheating		Unit Permanent Changes in Length
Deg. C.	Deg. F.	
500	932	0.00009
425	797	0.00031
375	707	0.00085
325	617	0.00116
300	572	0.00130
275	527	0.00143
226	440	0.00151

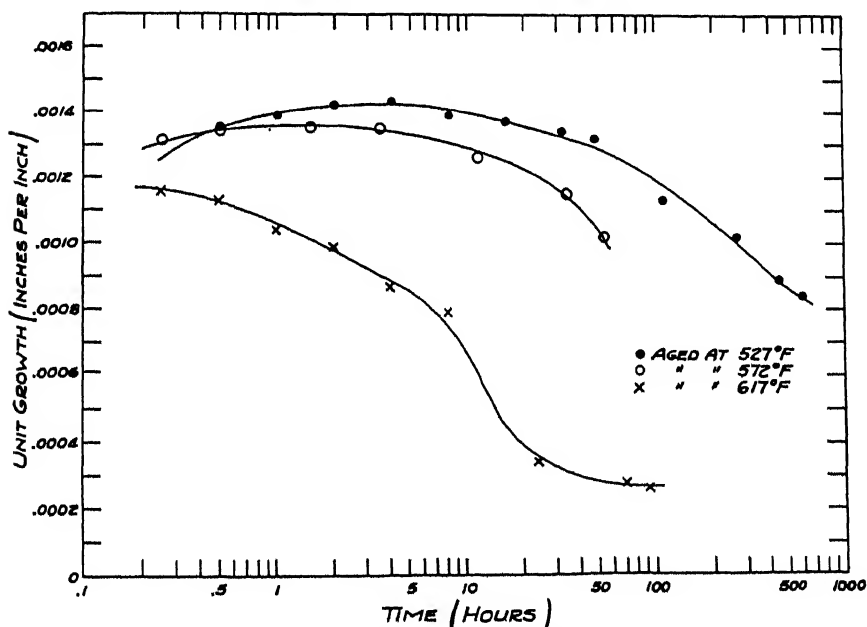
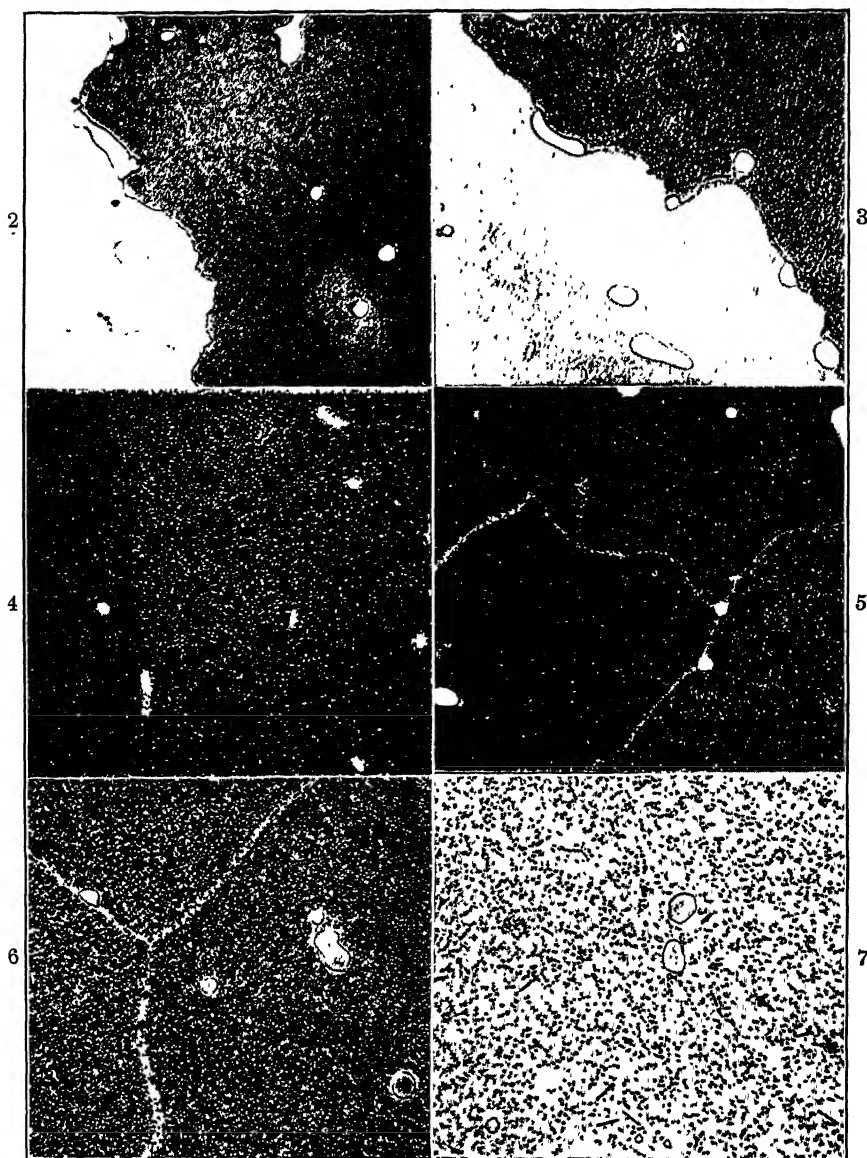


FIG. 1.—RATE AND MAGNITUDE OF GROWTH AT VARIOUS TEMPERATURES FOLLOWING RAPID COOLING FROM 1000° F. OF ALUMINUM ALLOY CONTAINING 6 PER CENT COPPER.

until maximum growth was obtained. Fig. 1 shows the progress of growth with time at three of the temperatures investigated. These curves are probably typical of the general growth-time curve. At the higher



FIGS. 2-7.—STRUCTURAL CHANGES IN ALUMINUM-COPPER SOLID SOLUTION ON REHEATING.

FIG. 2.—SAMPLE R-4431-1A. $\times 500$. 6 PER CENT CU ALLOY QUENCHED FROM 16 HR. AT 1000° F.

Etched with 2.5 per cent HNO_3 , 1.5 per cent HCl , 1.0 per cent HF .

FIG. 3.—SAMPLE R-4525-3. 6 PER CENT CU ALLOY QUENCHED AND AGED 5 MINUTES AT 572° F. UNIT GROWTH ABOUT 0.0012.

FIG. 4.—SAMPLE R-4431-4A. AGED $\frac{1}{2}$ HOUR AT 572° F. UNIT GROWTH 0.00134.

FIG. 5.—SAMPLE R-4431-4B. AGED $1\frac{1}{2}$ HOURS AT 572° F. UNIT GROWTH 0.00135.

FIG. 6.—SAMPLE R-4431-1B. AGED 21 HOURS AT 572° F. UNIT GROWTH 0.00103.

FIG. 7.—SAMPLE R-4431-3. AGED 92 HOURS AT 617° F. UNIT GROWTH 0.00026.

temperatures maximum growth is attained so rapidly as to make difficult the accurate determination of the initial portion of the curve; at the lower temperatures the time required to bring about contraction following the attainment of maximum growth is so great that the completion of the curve becomes tedious. The values given for maximum growth are therefore most accurate in the temperature range 200° (392°) to 260° C. (500° F.). Figs. 2 to 7 illustrate the changes in structure accompanying the density changes on reheating the quenched solid solution.

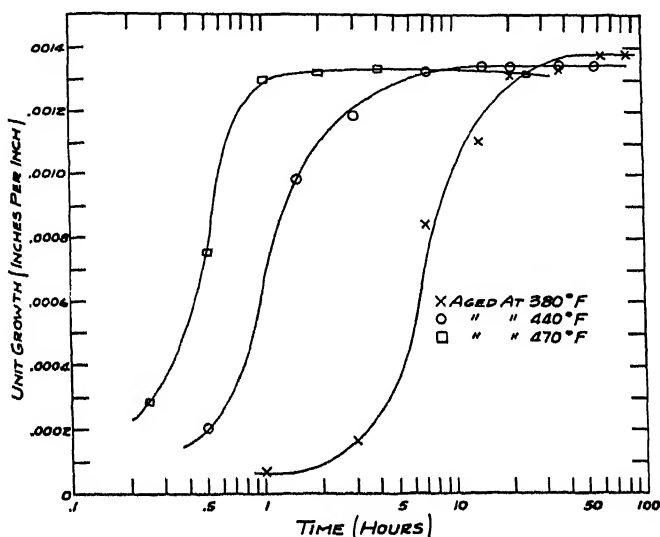


FIG. 8.—CURVES SHOWING RATE AND MAGNITUDE OF GROWTH AT VARIOUS TEMPERATURES FOLLOWING RAPID COOLING FROM 1000° F. OF ALUMINUM ALLOY CONTAINING 10 PER CENT COPPER.

The maximum growth decreases with increase in the temperature of reheating in accordance with the hypothesis stated in the foregoing paragraph. On the other hand, observations over a period of months at room temperature have revealed no regular changes in specific volume, suggesting that in most alloy systems there exists a minimum temperature below which the atomic lattice is too stiff to permit sufficient diffusion for precipitation, although Portevin and Chevenard⁷, using a highly sensitive dilatometer, have noted very small expansions in Al-Mg₂Si and contractions in Al-Cu alloys on aging at room temperature following quenching from a high-temperature solution treatment. These changes were of the order of 0.005 to 0.01 per cent, thus being too small to be noticed by the methods used in this investigation.

The lower limit in temperature for the practical determination of growth of aluminum alloys appears to be in the neighborhood of 300° F.

In most alloys, growth at this temperature takes place so slowly as to be of little practical importance in the application of the alloy and certainly of no interest with regard to bringing about complete growth prior to application. The upper limit in temperature, on the other hand, is fixed by the necessity for maintaining a high combination of mechanical properties. The curves of Figs. 8 and 9 give the progress of growth and hardness in a high-purity alloy containing 0.03 per cent iron, 0.02 per cent silicon, 10.14 per cent copper-aluminum. The alloy was cast in the form

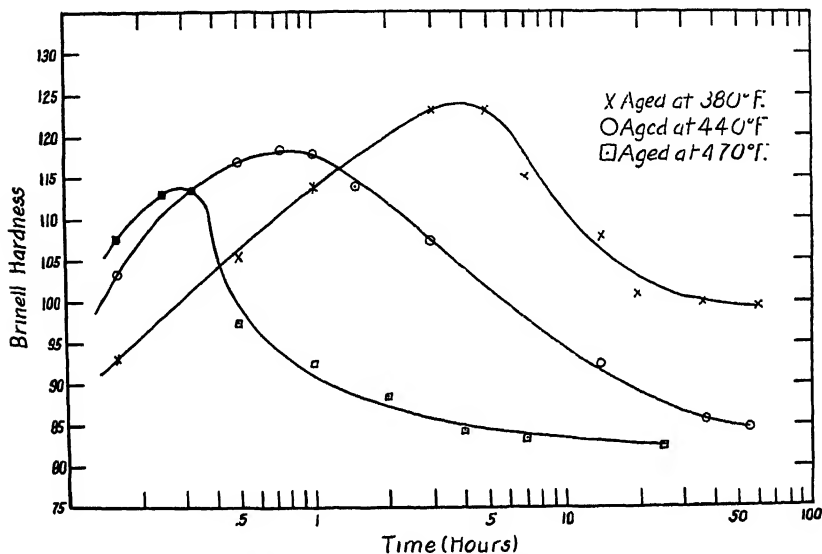


FIG. 9.—HARDNESS CHANGES OF SPECIMENS OF FIG. 3.

of water-cooled ingots. Cylinders were machined from the ingot, measured, heated at 538° C. (1000° F.) for 16 hr., quenched and reheated. Measurements were made at various periods during the reheating, as indicated by the points on the curves. The measurements were made at room temperature following cooling in water from the reheating temperature. Table 2 gives the data from which the growth curves were plotted.

Fig. 10 shows typical growth and hardness curves for commercial wrought 25S alloy. In Fig. 11 the log of the time required for the attainment of maximum hardness, as indicated by the curves of Fig. 9, is plotted against the values of maximum hardness and growth. A similar curve for the growth of an alloy containing approximately 7 per cent each of copper, nickel and silicon, is included.

Table 3 gives the maximum growth typical of the binary alloy systems of most importance in commercial aluminum alloys. These determina-

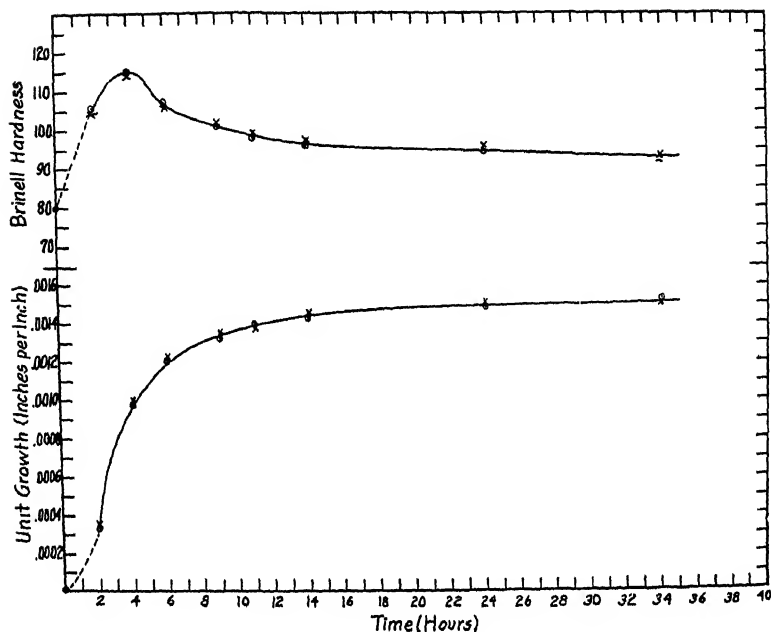


FIG. 10.—GROWTH AND HARDNESS CURVES FOR 25S ALLOY, REHEATED AS INDICATED FOLLOWING RAPID COOLING FROM A SOLUTION TREATMENT AT 960° F. Crosses and circles indicate determinations on two different specimens.

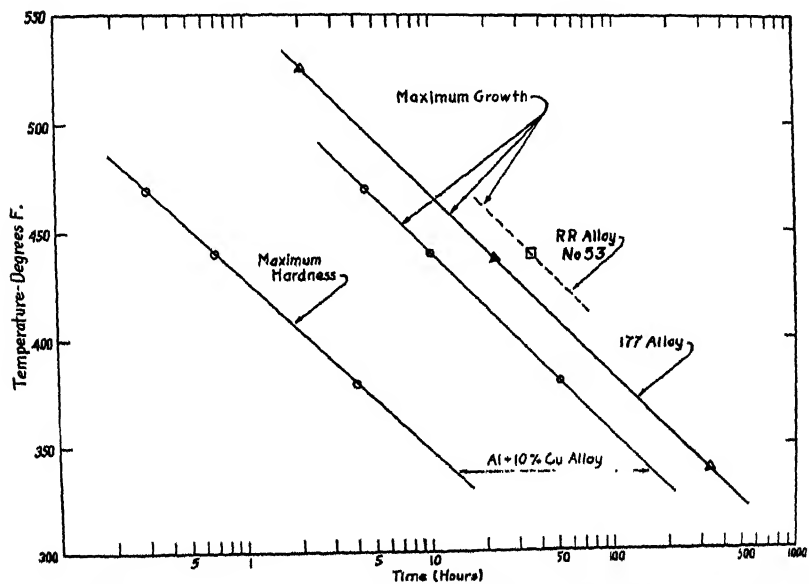


FIG. 11.—TIME REQUIRED AT VARIOUS TEMPERATURES TO REACH MAXIMUM HARDNESS AND MAXIMUM GROWTH FOR SEVERAL ALUMINUM ALLOYS.

tions were made in substantially the same manner as those on the 10 per cent copper alloy described above. In most cases the concentration of the alloying element is sufficient to provide a saturated solution at the solution heat-treating temperature, which was selected as near to the eutectic temperature as feasible. With magnesium and zinc, however, the concentrations are appreciably below the maximum solubility of these elements in aluminum at the eutectic temperature. The concentrations,

TABLE 2.—*Growth of a 10 Per Cent Copper Alloy at Various Temperatures*
CHILL-CAST ALLOY CONTAINING 10.14 PER CENT CU, 0.03 PER CENT FE, 0.02 PER CENT SI, QUENCHED IN BOILING WATER FROM 16 HR. AT 538° C. (1000° F.) AND REHEATED AT TEMPERATURES INDICATED

	Unit Growth		
Annealed (2 hr. at 343° C. (650° F.).....)	0 00033		
Heated 16 hr. at 538° C. (1000° F.) and quenched...	-0.0006*		
Reheated at.....	193° C. (380° F.)	226° C. (440° F.)	243° C. (470° F.)
Hr.			
0.25			0.00029
0.5		0.00021	0.00076
1.0	0.00008	0.00052	0.00130
1.5		0.00098	
2.0			0.00132
3.0	0.00017	0.00118	
4.0			0.00132
7.0	0.00084	0.00132	0.00132
14.0	0.00111	0.00134	
20.0	0.00131	0.00133	
25.5			0.00132
36.0	0.00133	0 00134	
55.0	0.00134		
60.0	0.00138		
84.0	0.00138		

* Minus sign indicates shrinkage.

however, are about the maximum utilized in industrial alloys. It will be noted that the maximum growth varies considerably between the different alloy systems. The temperature used for the determination of maximum growth was such as to permit the attainment of substantially complete growth in periods of time short enough to be commercially permissible. In every case the reheating was continued with periodic measurements until it was evident that maximum growth had been obtained.

It is to be expected that the commercial alloys would show growth of the same order of magnitude as that of the pure binary alloy systems. That this is true is indicated in the data of Table 4, giving the maximum

growth of some commercial alloys. It is to be understood, of course, that these values for maximum growth apply only to the specific temperature at which the determination is made. At higher and lower temperatures the amount of maximum growth will be less or greater in about the same ratio as indicated in Table 1 and curves of Figs. 1 and 3, for the variation in the amount of maximum growth with temperature, for 6 and 10 per cent copper alloys.

TABLE 3.—*Growth of Aluminum-alloy Solid Solutions*

Alloy System	Analysis, Per Cent				Temperature of Solution Treatment		Temperature of Reheating		Maximum Unit Growth
	Cu	Fe	Si	Others	Deg. C.	Deg. F.	Deg. C.	Deg. F.	
Al-Cu.....	6 08	0 03	0 09		535	995	226	440	0 0015
	10				535	995	226	440	0 0014
Al-Mg.....	0 02	0.18	0.07	Mg 10	426	800	204	400	0 0015
					426	800	188	370	0 0016
Al-Mg ₂ Si....	0.02	0.01	0.85	Mg 1.56	565	1050	226	440	Nil
Al-MgZn ₂	0.02	0.04	0.01	Mg { 1 57 Zn { 8.43	498	930	204	400	-0 0008*
Al-Ni.....	0.01	0.02	0.02	Ni 5.06	630	1166	226	440	Nil
Al-Si.....	0.02	0.02	1.79		570	1058	226	440	0.0016
			12.82		565	1050	226	440	0.00136
Al-Zn.....	0.02	0.05	0.01	Zn 10.03	498	930	204	{ 400	Nil
							100	{ 212	
							21	{ 70	

* Minus sign indicates shrinkage.

The variation in the amount of growth with composition, indicated in Tables 3 and 4, is again emphasized in the curve of Fig. 12. No. 122 alloy contains about 10 per cent copper, 1 per cent iron, 0.25 per cent magnesium and 0.5 per cent silicon, and has been used in the production of millions of automotive pistons. The curve of Fig. 12 illustrates the effect of variations in the magnesium concentration of this alloy on its maximum growth at 226° C. (440° F.). With increasing amounts of magnesium, the maximum growth decreased continuously, approaching zero growth at about 1.5 per cent magnesium.

Although there are similarities in progress of growth and hardening on reheating, there are also important differences, for example, maximum growth and maximum hardness occur at widely different times in the

TABLE 4.—*Growth of Commercial Alloys*

Trade Designation	Nominal Composition, Per Cent						Condition	Temperature of Reheating, Deg. F.	Maximum Unit Growth
	Cu	Fe	Si	Mg	Ni	Ti			
Alcoa:									
122	10.0	1 2		0 2			As chill-cast	340	0 0006
122	10 0	1 2		0 2			Solution treatment, 960° F. ^b	340	0.0009
132	0.8	0 8	14.0	1.0	2 5		As chill-cast	440	0.0003
132	0.8	0 8	14 0	1 0	2 5		Solution treatment, 980° F.	440	0.0004
142	4.0			1 2	2 0		As chill-cast	440	0.0001
142	4.0			1 2	2 0		Solution treatment, 960° F.	440	0 0001
195	4 0						Solution treatment, 960° F.	440	0.0015
355	1.25		5 0	0 5			Solution treatment, 980° F.	440	0 0008
356			7 0	0 3			Solution treatment, 1000° F.	440	0 0008
220				10.0			Solution treatment, 810° F.	370	0 0016
177	7.0		7 0		7 0		Solution treatment, 940° F.	340	0 0009
32S			12.0	1.0	0.8		Solution treatment, 960° F.	400	0 0006
25S	4 5		0.8		(0.8 Mn)		Solution treatment, 960° F.	440	0.0015
A51S			1 0	0 6	(0 25 Cr)		Solution treatment, 980° F.	440	0 0001
17S	4 0			0.5	(0 5 Mn)		Solution treatment, 930° F.	440	0.0006
18S	4 0			0.5	2.0		Solution treatment, 960° F.	440	0.0005
R.R.:									
53 ^a	2 3	1 95	1.25	1 68	1.37	0 12	Solution treatment, 930° F	440	0 0004
Alcoa:									
43			5 0				As chill-cast	440	0 0009
43			5 0				Solution treatment, 1000° F.	440	0 0016
47			12.5				As chill-cast	440	0 0003
47			12 5				Solution treatment, 1000° F.	440	0 0014

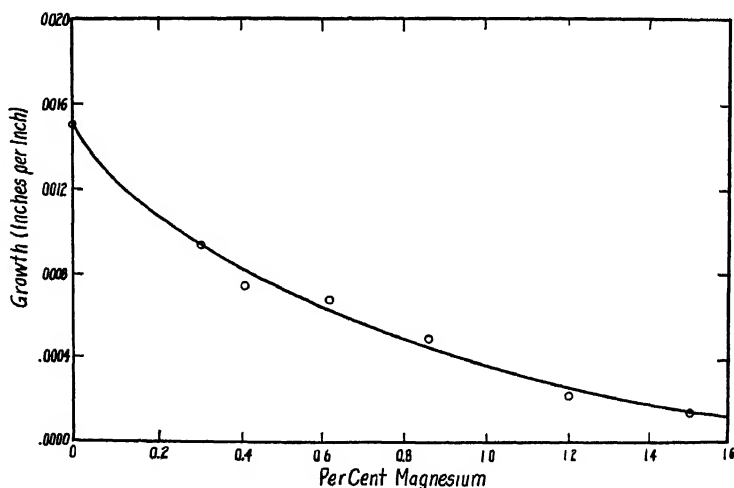
^a Composition by analysis^b Solution treatment indicates rapidly cooled from a commercial solution heat-treatment at temperatures indicated.

FIG. 12.—EFFECT OF MAGNESIUM CONCENTRATION ON MAXIMUM GROWTH ON REHEATING AT 400° F. OF 122 ALLOY, FOLLOWING RAPID COOLING FROM SOLUTION TREATMENT AT 960° F.

reheating cycle. In applications where even the small amount of growth encountered in most aluminum alloys is undesirable, a compromise must be made between maximum mechanical properties and complete dimensional stability. Table 5 gives the mechanical properties of some commercial heat-treated alloys in the conditions of substantially maximum mechanical properties and substantially complete freedom from growth. Although some sacrifice in mechanical properties is necessary, if complete stability is desired, still the properties of the alloys subjected to a

TABLE 5.—*Properties of Commercial Alloys*

Alloy	Conditions	Treatment	Average Properties, Production Tests			Specification Values Tensile Strength (minimum), Lb. per Sq. In.
			Tensile Strength, Lb. per Sq. In.	Elong- ation, Per Cent in 2 In.	Brinell Hardness, 500 Kg., 10 Mm.	
122-T551	Chill-cast	Aged ^a	35,900		125-150	30,000
122-T552	Chill-cast	"Degrowthed" ^b	33,300		100-125	27,000
132-T65	Chill-cast	Solution treatment and aged ^c	35,500		120-150	32,000
132-T7	Chill-cast	Solution treatment and "degrowthed" ^d	36,500	0.6	95-120	30,000
132-T65	Sand-cast	Solution treatment and aged	34,300	0.5	100-120	30,000
132-T7	Sand-cast	Solution treatment and "degrowthed"	32,700	0.5	85-115	25,000
355-T5	Sand-cast	Aged	27,800	1.6	65- 85	26,000
355-T59	Sand-cast	"Degrowthed"	28,000	1.9	50- 70	23,000
A355-T51	Sand-cast	Aged	27,700	1.2	60- 80	25,000
A355-T59	Sand-cast	"Degrowthed"	25,000	1.9	50- 70	23,000
356-T51	Sand-cast	Aged	26,500	2.2	50- 70	23,000
356-T59	Sand-cast	"Degrowthed"	26,200	2.3	45- 65	23,000

^a Heated at relatively low temperatures in as-cast condition to bring about precipitation-hardening.

^b Heated in as-cast condition at elevated temperatures for periods of time sufficient to bring about substantially complete growth.

^c Rapidly cooled from high-temperature solution treatment, then reheated as in footnote *a*.

^d Rapidly cooled from high-temperature solution treatment, then reheated as in footnote *b*.

stabilizing treatment are considerably higher than with no heat-treatment whatever.

DISCUSSION OF RESULTS

It seems obvious that precipitation-hardening and the volume changes occurring on reheating supersaturated solid solutions are both manifestations of decomposition of the solid solution. The usual course of precipitation-hardening at temperatures above room temperature appears to consist in an initial decrease in hardness, followed by a relatively rapid increase to maximum hardness. The hardness curves in this paper are not sufficiently detailed in the first stages of reheating to show the initial softening. The phenomenon, however, has been observed sufficiently

frequently to leave little doubt as to its universality. The hardness then declines at first fairly rapidly and then more slowly. No reversals in the initial stages of the growth-time curves have been observed at any temperature at which growth has been observed (the lowest temperature of observation being 100° C. (212° F.). Under any conditions wherein growth may be observed, it appears to progress continuously at first at approximately a linear rate, which decreases as maximum growth is approached, and after a certain definite maximum growth has occurred contraction proceeds at a high or low rate, depending on temperature of reheating.

Most important from the commercial viewpoint is the fact that in all the aluminum alloys examined, under isothermal conditions, growth takes place much later than hardening in point of time. This obviously precludes the possibility of obtaining simultaneously the maximum combination of mechanical properties and complete freedom from growth. It will be seen, therefore, that while the hardness and mechanical properties are very sensitive to variations in the physical condition, such, for example, as the size of the particles of the precipitating phase, growth on the other hand occurring as it does, almost simultaneously with changes in lattice parameter, appears to be more intimately related to the solid solution matrix than to the precipitating phase.

It should be observed, however, that it is not lattice-parameter changes alone that govern the amount of growth. In the aluminum-base magnesium alloys, for example, the solution of magnesium in the aluminum lattice brings about a marked expansion of the lattice, accompanied, however, by an increase in density. On reheating to relatively low temperatures, growth or a decrease in density occurs accompanied by contraction of the lattice parameter. This probably should be taken merely as an indication that the relative density of magnesium in solid solution in aluminum is higher than in the precipitated phase.

Consideration of the structural changes accompanying growth and hardening on reheating the aluminum-copper solid solution is interesting. The print in Fig. 2 shows the structure of the solid solution. Reheating at relatively low temperatures [below 177° C. (350° F.)] until maximum hardness is attained brings about relatively minor visible changes in structure. The progress of growth, however, is accompanied—especially as maximum growth is approached—by relatively gross changes in microstructure, which are most conveniently followed with temperatures of reheating in the neighborhood of 300° C. (572° F.). The first few minutes at temperature (Fig. 3) produces definite precipitation along the grain boundaries accompanied by a reduction in the contrast between grains. The grain contrast decreases and the entire structure etches to a darker tone as growth proceeds until at maximum growth (Fig. 5) the darkest tone and minimum grain contrast are achieved. As reheating continues

beyond this stage the etched structures become lighter in color, agglomeration proceeds visibly in the grain boundaries, and, inferentially, within the grains until discrete particles can be discerned throughout the structure (Fig. 7). It is interesting that the particles of the precipitated phase must become fairly large before a condition of relative stability is reached. It is not inconceivable that the condition of maximum growth is the condition of maximum surface area of CuAl_2 particles. In other words, at maximum growth or minimum density the boundary between the CuAl_2 lattice and the aluminum lattice may be definite, indicating discrete particles of CuAl_2 . At maximum hardness, on the other hand, boundaries may be considerably less definite; the transition from the CuAl_2 lattice to aluminum solid solution lattice perhaps passing through several stages. For example, at the center of precipitation the CuAl_2 lattice only is probably present, moving away from this center, a gradually increasing concentration of aluminum is encountered until the lattice of the aluminum solid solution predominates. These remarks refer only to majority effects. It is known, for example, that relatively large particles of CuAl_2 with definite boundaries exist at least in the grain boundaries at, and even prior to, maximum hardness. It is probable, however, that these particles have a relatively small hardening effect.

Theoretical aspects of the connection of growth with other precipitation phenomena will not be further considered here. There is no doubt, however, of its fundamental importance in a complete picture of precipitation-hardening. The effect of magnesium on the hardening of the aluminum-copper solid solution, which has been noted by numerous investigators, and its effect on the density changes occurring during breakdown of the aluminum-copper solid solution, as indicated in Fig. 11, is undoubtedly an illustration of this relationship.

Table 2 shows that the potential growth of the various aluminum-alloy solid solutions varies over a considerable range from practically zero for aluminum-magnesium silicide to a unit growth of 0.0016 for the aluminum-magnesium and aluminum-silicon solid solutions. It should also be noted that the rate of growth differs widely, as indicated by the position of the growth lines for the various alloys in the curves of Fig. 11. Thus the time to reach complete growth at any specific temperature with the range investigated is less for the 10 per cent copper alloy than for the alloy containing 7 per cent each of copper, nickel and silicon, which in turn reaches a condition of complete growth much more quickly than the R.R. alloy. These variations in rate are of considerable practical importance and must be taken into consideration in the design of commercial heat-treatments. As the temperature is reduced, the time required to attain complete growth increases enormously. Observations have not been made over a long enough period of time at room temperature to satisfactorily establish whether growth occurs at such low tem-

peratures. Preliminary measurements of some alloys at 100° C. (212° F.) indicate that in most alloy systems years will be required for the attainment of complete growth at this temperature. It is obvious that changes in dimensions of the ordinary structures at temperatures up to 100° C. during the life of the structure need not generally be considered. In fact, the magnitude of growth is such that it need be considered even at elevated temperatures only in relatively few specific applications.

It should perhaps be emphasized that changes of dimension during machining, assembly, or service life of a structure does not necessarily, or usually, imply growth. There are at least three other reasons for changes in dimension, which may be much more effective than growth. These are: (1) thermal expansion, (2) internal stress and (3) external stress. A change in temperature of 37.8° C. (100° F.) will bring about a change of dimension practically equivalent to the maximum growth encountered in any aluminum-alloy system. Similarly, the presence of a stress, either external or internal, of about 15,000 lb. per sq. in. will bring about a deformation substantially equivalent to the maximum growth encountered in aluminum alloys. Internal stress of this order of magnitude may be quite readily developed by improper heat-treatment or cold-working.

It is probable that practically all distortion encountered during machining is due to relief of internal stress rather than to growth. The possibility of developing internal stress by quenching has been treated elsewhere.⁸ It was pointed out that castings could be heat treated under conditions such as would insure practical freedom from internal stress. In case, however, the proper rate of quenching is not applicable, internal stress may be relieved by reheating in much the same manner as growth may be brought about. Sufficient investigational work, however, has been carried on in these laboratories to indicate that complete relief of internal stress requires even higher temperatures or much longer periods of time than are necessary to bring about complete growth. Thus, for example, with an internal stress of about 5000 lb. per sq. in., reheating 8 hr. at 226° C. (440° F.), will reduce this stress about 30 per cent; 20 hr. at 226° C. (440° F.) will increase the percentage of reduction in stress to about 38 per cent, while a reduction to 75 per cent of the original value will require about 500 hr. at 226° C. (440° F.). At this temperature, complete growth is attained in the alloy investigated within about 15 hr. It should not, therefore, be assumed that a casting that has been completely "degrowthed" (stabilized) will be entirely free from distortion on machining. While it is true that the ordinary "degrowth" treatments carried out in the neighborhood of 226° C. bring about some relief of internal stress and some evidence is available indicating that the initial 25 per cent reduction in internal stress is by far the most important in bringing about practical stability, still

under some conditions sufficient internal stress may be still present to cause distortion.

In some circumstances growth may be desirable; for example, the temperature of operation of aluminum-alloy pistons in many internal-combustion motors is such that growth may take place. It has been demonstrated that with the proper selection of alloy the growth that takes place under a specific set of conditions may approximately compensate for the wear incidental to operation.

SUMMARY

1. The "growth" of a number of aluminum alloys on reheating in the temperature range 175° (346°) to 230° C. (446° F.) following rapid cooling from a solution heat-treatment has been determined.

2. The amount of growth of the alloys examined varies between zero and 0.16 per cent, depending on composition and heat-treatment.

3. The rate of growth under isothermal conditions varies over a relatively wide range with variations in composition.

4. At a specific temperature of reheating, maximum mechanical properties and maximum growth occur after different periods of time at temperature, the attainment of maximum growth requiring considerably longer periods of time than maximum hardness.

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DISCUSSION

(R. M. Brick presiding)

R. M. BRICK* AND A. J. SMITH,* New Haven, Conn. (written discussion).—The authors have found it expedient to study the growth occurring during precipitation principally as a problem of commercial importance. At the same time, the growth process furnishes an additional method of attack on the theoretical aspects of precipitation-hardening, since, as Kempf and Hopkins point out, density changes are intimately associated with the separation of a second phase. It is not intended to discuss the authors' results from the age-hardening viewpoint, but rather to examine their data as connected with the identity of the precipitating solute. In this respect, Fig. 1 is most interesting. X-ray lattice-parameter data of this laboratory on comparable alloys show that at 617° F. precipitation is completed slightly after the point of maximum growth; at 572° F., precipitation is complete just before the point of maximum growth and at 527° F., noticeably before the maximum growth. No further

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change in parameter of the matrix, assuming the specimen to be free from strain, takes place during the subsequent process of contraction shown in the figure. The contraction must then be associated with a change of the second or precipitated phase. Wassermann and Weerts have recently shown that the precipitated phase at temperatures below 572° F. has not the normal CuAl_2 or θ phase structure but a much larger θ' structure. Fink and Smith have shown (p. 284) that the θ' structure does occur and can explain the anomalous density changes during precipitation found in the literature. The points of maximum growth and maximum contraction shown in Fig. 1 have been calculated into densities on the assumption of a 5 per cent copper content which will actually give only a slight relative error. Then the proportions of the θ' and θ phases were calculated and the results tabulated (Table 6).

TABLE 6.—*Proportions of θ and θ' Phases**

	Calculated Density	θ' , Per Cent	θ , Per Cent
Complete solution.	2.8030		
¼ hr. 617° F., maximum growth.	2.7932	70	30
96 hr. 617° F., contraction.	2.8007	35	65
2 hr. 572° F., maximum growth	2.7918	77	23
50 hr. 572° F., contraction.. . . .	2.7944	65	35
4 hr. 275° F., maximum growth.	2.7910	81	19
600 hr. 275° F., contraction	2.7958	58	42

* On the basis of densities, 3.99 for θ' and 4.35 for θ , as given by Fink and Smith (pp. 291 and 292, this volume).

The figures given are approximations based on the known parameter and density changes. The proportions of θ' and θ are based on a calculated density of 2.787 grams per c.c. for the 5 per cent alloy with 100 per cent θ' and 2.808 grams per c.c. with normal CuAl_2 . It should be noted that with 100 per cent θ' the growth would be 0.0019 in. per inch, a value higher than any found experimentally by Kempf and Hopkins. On the other hand, if normal CuAl_2 were completely precipitated, there would be a contraction of 0.0006 in. per inch.

The density changes accompanying precipitation in several aluminum alloys have been studied in this laboratory. Table 7 shows the parameter and volume changes in a forged aluminum-magnesium alloy of high purity containing 8.2 per cent Mg.

TABLE 7.—*Changes in Forged Aluminum-magnesium Alloy Containing 8.2 Per Cent Magnesium*

Treatment	Parameter	Density	Growth	Hardness
Air-cooled from 450°C.	4 0800	2.5874		75
Heated 1 hr. at 210°C.	4 0800	2.5874		74
Heated 8 hr. at 210°C.	4.0804	2.5875		78
Heated 25 hr. at 210°C.	4.0789	2.5874		82
Heated 60 hr. at 210°C.	4 0734	2.5863	0.0001	86
Heated 120 hr. at 210°C.		2.5823	0.0007	88
Heated 200 hr. at 210°C.	4 0524	2.5806	0.0009	86

From these data, the calculated density of the precipitating phase appears to be approximately 2.155 grams per c.c., based on the compound formula Mg_2Al_3 . With further X-ray studies, it is hoped that the second phase will be positively identified.

L. W. KEMPF.—It is interesting to note from the density calculations that the precipitate was not completely converted to CuAl_2 under any of the conditions investigated.

Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy

BY WILLIAM L. FINK, * ASSOCIATE MEMBER A.I.M.E., AND DANA W. SMITH, * JUNIOR MEMBER

(New York Meeting, February, 1936)

MANY investigators have attempted to determine the true nature of the internal changes taking place during aging. Merica, Waltenberg and Scott^{1†} were the first to propose a theory of age-hardening. They attributed the age-hardening of duralumin to the precipitation of minute particles of the compound CuAl_2 . Later Zay Jeffries and R. S. Archer² augmented the above theory by suggesting that the small CuAl_2 particles acted as "keys" causing "slip interference." Many other investigators³ have devoted much time to the mechanism of age-hardening, some corroborating the "precipitation" and "slip interference" theory, others coming to different conclusions because of effects that to them seemed unexplainable by the early theories; e.g., the increase of electrical resistance upon aging, the fact that no change in lattice parameter could be detected during the early stages of aging even at elevated temperatures, and the fact that the density did not change as would be predicted.

In 1932, Merica revised⁴ his earlier precipitation theory to take care of these presumably anomalous effects. This revised theory, the "knot" theory, assumes that substantial age-hardening occurs before actual precipitation of solute as discrete particles. The assumed mechanism is one of diffusion of solute atoms into groups forming distorted regions which act as "hard" spots and cause slip interference. These "knots" are assumed to have approximately the same lattice arrangement as the solvent.

The anomalous behavior of lattice parameter, density, and electrical conductivity, require a modification of the simple precipitation-hardening theory, only if it is assumed that the precipitation of minute particles during aging has the same effects on these properties as the formation of large particles under equilibrium conditions. Data obtained by the authors in the study of the aluminum-magnesium system⁵ indicated that

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† References are at the end of the paper.

this assumption is not tenable for lattice-parameter measurements. Consequently a series of experiments has been initiated to study the mechanism of age-hardening in various aluminum alloys. The present paper presents certain data obtained up to the present time on an aluminum-copper alloy.

Material.—The aluminum used in the preparation of the aluminum-copper alloy contained less than 0.01 per cent each of iron, silicon and copper. The copper was a high-grade cathode copper containing impurities detectable by spectrographic analysis but not chemically determinable.

Preparation of Alloy.—Approximately 4 kg. of the aluminum was melted in a plumbago crucible in an electric furnace and the copper was added. The melt was thoroughly stirred with a graphite rod and fluxed with chlorine gas before casting. The metal was cast in the form of a sheet ingot in a cold iron tilting mold (approximately 200 by 165 by 40 mm.) and into small chill-cast slabs for chemical analysis (75 by 40 by 5 mm.).

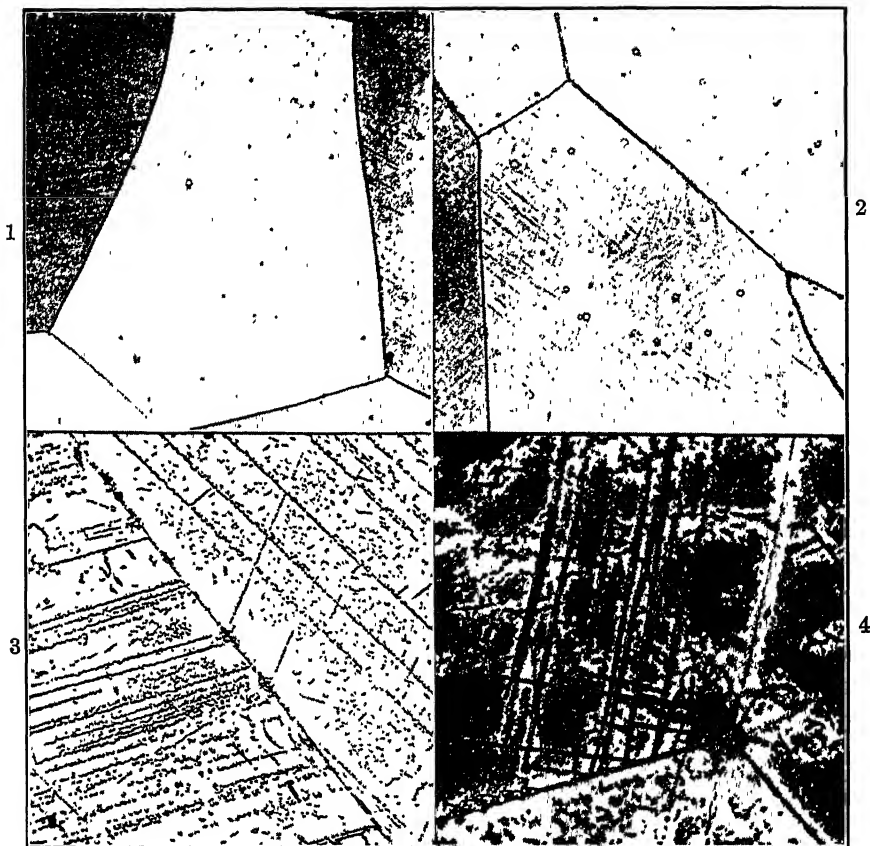
The chemical analyses were made upon drillings from the analysis slabs. The analytical methods used were those described in "Chemical Analysis of Aluminum," published by Aluminum Company of America. The composition was found to be: copper 5.17, silicon 0.01 and iron 0.01 per cent.

In order to insure homogeneity the material received two heatings at 495° C. for a total time of 14 hr. during the hot-rolling of the ingot to a thickness of 6.4 mm. The sheet was then cold-rolled to a thickness of 3.2 mm. Small specimens approximately 12 by 12 mm. to be used for microscopic examination and lattice-parameter measurements were cut from this sheet and the remainder of the sheet was further cold-rolled to a thickness of 1.6 mm. and cross-grained tensile specimens were machined with a formed milling cutter.

All of the specimens were heated for 20 hr. at 540° C., quenched in cold water and subsequently aged at various temperatures and for various times.

Microscopic Examination.—All of the specimens for microscopic examination were polished with unusual care to avoid defects such as polishing pits and surface flow. They were then etched by the most satisfactory procedure that we have yet found for revealing precipitate in aluminum-copper alloys; a method that was recently developed by F. Keller⁶, which consists in first immersing the specimen in a 25 per cent solution of nitric acid at 70° C., washing it in water and then immersing it in a solution containing 0.5 grams of sodium fluoride, 1 c.c. of concentrated nitric acid, 2 c.c. of concentrated hydrochloric acid per 100 c.c. of solution. The time required in each solution varies with the aging treatment that the sample has received.

Using the procedure just described it was possible to reveal evidences of precipitation in the very early stages of age-hardening, not only at grain boundaries but within the grain as well. The first evidences of precipitation were observed in specimens aged either 3 months at room



FIGS. 1-4.—ALUMINUM-COPPER ALLOY (5.17 PER CENT COPPER) HEATED 20 HR. AT 540° C., QUENCHED IN WATER AND AGED.

Etched in 25 per cent HNO_3 at 70° C., washed, and then etched in a solution containing: NaF , 0.5 gram; HNO_3 (conc.), 1.0 c.c.; HCl (conc.), 2.0 c.c.; H_2O , 97.0 c.c.

FIG. 1.—AGED 3 MONTHS AT ROOM TEMPERATURE, $\times 100$.

FIG. 2.—AGED $\frac{1}{2}$ HR. AT 160° C. $\times 100$.

FIG. 3.—AGED $2\frac{1}{4}$ HR. AT 200° C. $\times 500$.

FIG. 4.—AGED 256 HR. AT 160° C. $\times 500$.

temperature, or 1 hr. at 100° C., or 30 min. at 160° C., or 15 min. at 200° C. With these aging times the actual precipitated particles were not resolved but the planes upon which precipitation had taken place were clearly brought out, as shown in Figs. 1 and 2. Longer aging time resulted in the growth of particles to a size that could be clearly resolved as shown in Figs. 3 and 4.

It is evident that the first visible precipitation takes place on certain crystallographic planes. The precipitate that formed at 160° C. was on the planes along which slip occurred when the specimen was subsequently squeezed in a vice. Previous work has shown that the slip occurs on the {111} plane. However, the identification of the plane upon which precipitation occurred is now being repeated by X-ray methods on single crystals of this aluminum-copper alloy.

Lattice-parameter Measurements.—The same polished surfaces that were used for microscopic examination were also used for the measurement of lattice parameter by the back-reflection method. No change in lattice

TABLE 1.—*Age-hardening Data on Aluminum-copper Alloy
(5.17 Per Cent Cu) Aged at 100° C.*

Aging Time, Hr. at 100° C.	Yield Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Lattice Parameter, Å.
0	25,300	18	4.0305
½			4.0304
1			4.0302
2			4.0303
4			4.0304
8			4.0305
24	30,800	16.5	4.0303–4.0610
34			
48	31,150	14.3	
64			4.0299–4.0623
96	32,350	12.0	
128			4.0309–4.0634
192	31,800	8.8	
256			4.0305–
414	32,100	7.5	
768	33,750	6.5	

parameter could be detected until the specimen had aged for a much longer time than was necessary to produce visible precipitation. The very first evidences of change in lattice parameter occurred after aging for either 34 hr. at 100° C., or 4 hr. at 160° C. or ½ hr. at 200° C. The lattice parameter did not change uniformly throughout the entire specimen. Only a small percentage of the specimen suffered any change in lattice parameter during the early stages and the original lattice parameter persisted throughout most of the specimen. As the aging time increased the percentage of the specimen that suffered parameter change gradually increased but some material of the original parameter existed after 256 hr. at 100° C., after 128 hr. at 160° C., and after 16 hr. at 200° C. These parameter changes are in agreement with the previous results of

Sachs and others. The lattice-parameter measurements are summarized in Tables 1, 2 and 3 and in Figs. 5, 6 and 7.

TABLE 2.—*Age-hardening Data on Aluminum-copper Alloy
(5.17 Per Cent Cu) Aged at 160° C.*

Aging Time, Hr. at 160° C.	Yield Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Lattice Parameter, Å.
0	25,300	18	4 0305
¼	26,200	19	4.0304
½	25,850	18 8	4.0305
1	28,200	19	4 0305
2	28,150	14 3	4 0304
4	29,400	12 5	4 0304-4.0404
8	31,400	11 5	4 0305-4 0436
16	34,000	8 0	4 0313-4.0435
32	36,250	4 5	4.0308-4.0435
64	40,850	4 0	4 0306-4 0467
128			4.0344-4.0465
144	41,700	2.5	
256			4 0235-4.0505
258	44,450	2.5	

TABLE 3.—*Age-hardening Data on Aluminum-copper Alloy
(5.17 Per Cent Cu) Aged at 200° C.*

Aging Time, Hr. at 200° C.	Yield Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Lattice Parameter, Å.
0	25,300	18	4 0305
½			4.0305
¼			4 0306
½	25,850	13 5	4 0304-4.0407
1	31,750	9 8	
1¼			4.0307-4.0407
2	34,600	6 8	
2¼			4.0318-4.0437
4	36,400	5 5	4.0304-4.0407
8	39,150	5.0	4.0305-4.0436
16	40,000	4 3	4 0300-4.0401
32			4.0401
64			4 0409
128			4.0409
256			4.0412

Tensile Tests.—Previous work has shown that the most reliable criteria of the extent of age-hardening are yield strength and elongation. Consequently these properties were determined as a function of aging time for

this alloy. The values are given in Tables 1 to 3 and in Figs. 5 to 7. All of the values were determined on standard A.S.T.M. cross-grain specimens. The specimens were tested in an Amsler testing machine equipped with self-aligning grips⁷. The yield strength was determined from the stress-strain curve drawn by an electric recording extensometer⁸.

Identification of Precipitating Phase.—Recently Wassermann and Weerts⁹ have shown that the copper-rich phase that precipitates in a 5 per cent copper alloy at 200° C. has a different crystal structure (which we will denote by θ') from the equilibrium phase θ . They did not determine the complete crystal structure but they did report that the unit cell was tetragonal of the dimensions $a_0 = 8.2$ Å., $c_0 = 11.6$ Å. and $c/a = 1.41$, and that this cell probably contains 16 atoms of copper and 32 atoms of aluminum.

Debye-Scherrer X-ray patterns made from aged samples of the 5 per cent copper alloy used in this work yielded reflections checking the more intense reflections reported by Wassermann and Weerts for their "transition phase" (θ') as shown in Table 4.

TABLE 4.—*Interplanar Spacings of Transition Phase*

Indices	$d(hkl)$ calculated from Wassermann and Weerts results	$d(hkl)$ (Fink and Smith)
(202)	0.3335	0.3275
(224)	0.2042	0.2045
(206)	0.1756	0.1725 (broad)
(242)	0.1737	
(408)	0.1174	0.1172 (broad)
(624)	0.1176	

DISCUSSION OF RESULTS

The curves of Figs. 5, 6 and 7 summarize the data on elongation, yield strength, lattice parameter and the time required for the first evidences of precipitation. It is evident that precipitation has occurred before any change in lattice parameter can be detected and before the yield strength or elongation has suffered any substantial change. Even under the most favorable conditions one could scarcely hope to reveal the very first particles of precipitate. Consequently it seems probable that the first changes in elongation and yield strength may be accounted for by actual precipitation of submicroscopic particles. It seems unnecessary therefore to attempt to complicate or modify the theory of Merica, Waltenberg and Scott that age-hardening is caused by the precipitation of particles from the supersaturated solid solution.

The anomalous behavior of electrical resistivity and density during the aging of aluminum-copper alloys might be accounted for merely by the size of the precipitating particles. For example, it is conceivable

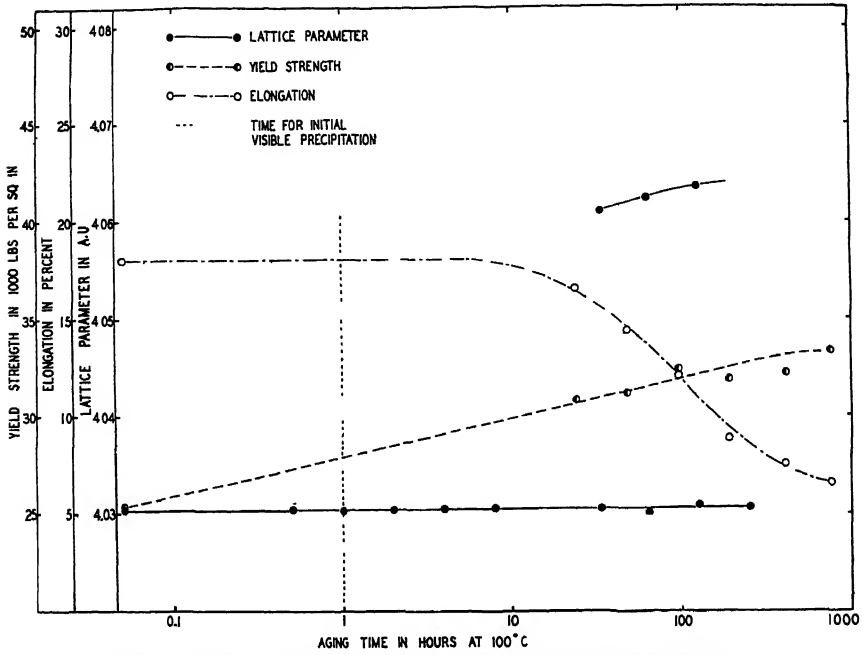


FIG. 5.—PLOT OF AGE-HARDENING DATA CONTAINED IN TABLE 1.

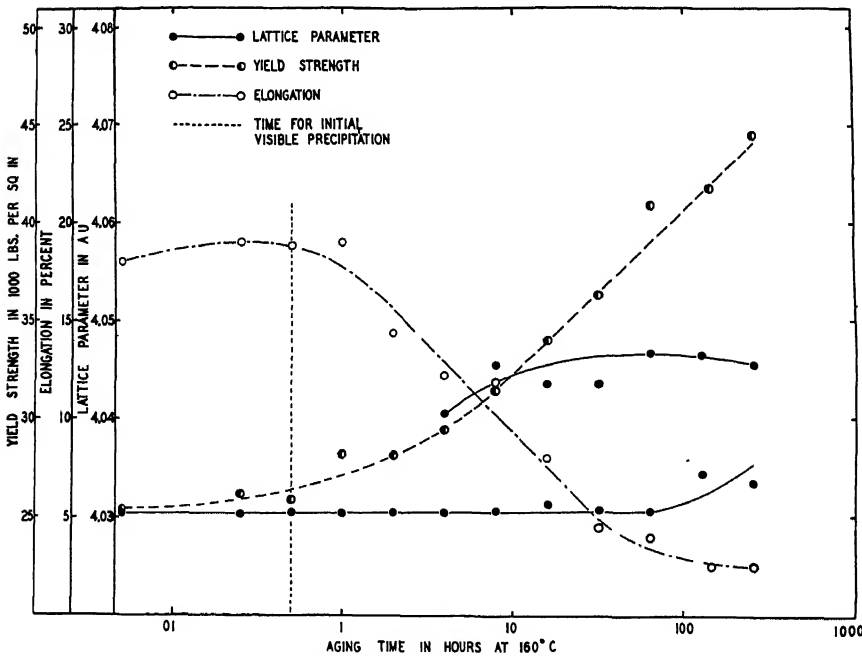


FIG. 6.—PLOT OF AGE-HARDENING DATA CONTAINED IN TABLE 2.

that very minute submicroscopic particles of copper-rich constituents would be more effective in interfering with the electron flow through the metal than copper atoms arranged on the aluminum lattice. It is also conceivable that the region immediately adjacent to each small particle would represent a region of lower density because the atoms would not fit on the lattice of the aluminum solid solution nor on the lattice of the precipitated particles. However, particle size is not the only possible

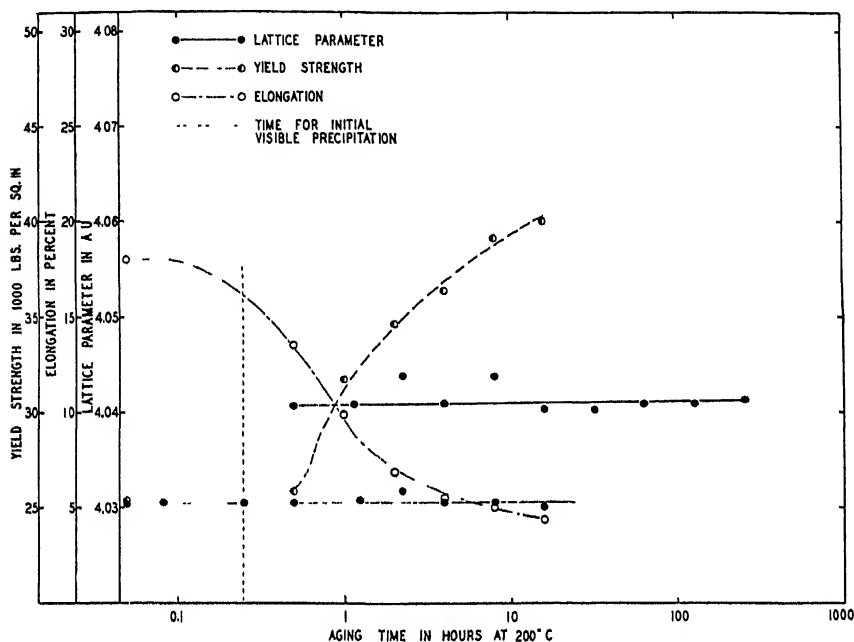


FIG. 7.-PLOT OF AGE-HARDENING DATA CONTAINED IN TABLE 3.

factor. The properties of the intermediate phase (θ'), which has been identified, may account for some of the behavior previously considered anomalous.

For example, it has been known for some time that density changes suffered by aluminum alloys upon aging could not be accounted for solely by the precipitation of the equilibrium phase. Considering, now, the aluminum-copper alloys with θ' as the precipitate, the density changes may be explained without consideration of particle size. For example: the density of a 5 per cent copper alloy is 2.803 grams per cubic centimeter if the copper is all in solid solution in the aluminum lattice. If, upon aging, the copper-rich precipitating phase is θ (density 4.35 grams per c.c.) the density of the aged alloy will be 2.796 grams per cubic centimeter. This difference in densities between the "as-quenched" and "as-aged" conditions would only account for approximately one-half of the observed change in density upon aging at 225° C. On the other hand, if θ'

(density 3.99 grams per c.c.) is the precipitate, the density of the aged alloy will be 2.787 grams per cubic centimeter. This difference would account for slightly more than the observed change (at 225° C. aging temperature); however, in making these calculations it was assumed that precipitation was complete and that only θ' was formed. It is very probable that neither of these assumptions is true and a slightly more dense aged material would result if precipitation were not complete or (and) if some θ' transformed to θ .

Another observation has been that changes in density are largely dependent upon the aging temperature; that is, aging at low temperatures results in greater changes in density (requiring much longer times) than aging at higher temperatures. This is in accordance with the above assumptions, since it is more likely that θ' would be likely to partially transform to θ at higher aging temperatures.

The increase in density that occurs when the aging is prolonged beyond the point of minimum density may be accounted for by the transition of θ' to θ as well as by the growth of the precipitated particles.

CONCLUSIONS CONCERNING AGING OF ALUMINUM-COPPER ALLOY

1. Lattice parameter is not changed by precipitation of minute particles during age-hardening as it is by precipitation under equilibrium conditions.

2. Precipitation can be observed microscopically before the aging has progressed far enough to change the yield strength and elongation substantially.

3. The anomalous changes in density can be explained by particle size or by the precipitation of a transition phase (θ') which has been identified by Wassermann and Weerts and confirmed by the authors.

4. There now seems to be no justification for modification or complication of the theory of precipitation-hardening advanced by Merica, Waltenberg and Scott.

ACKNOWLEDGMENT

The authors express their appreciation to Mr. C. J. Walton, who prepared all the specimens for microscopic examination; to Mr. H. V. Churchill, under whose direction the chemical analyses were made; and to Mr. R. L. Templin, under whose direction the tensile tests were made.

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DISCUSSION

(F. N. Rhines presiding)

R. M. BRICK* AND A. J. SMITH,* New Haven, Conn. (written discussion).—The section of this study devoted to the identity of the precipitating phase is of particular interest in that it focuses attention on an often neglected factor of precipitation studies. The normal CuAl_2 structure as given by Friauf has not adequately explained the carefully determined changes in density occurring during precipitation. The authors, using the transitional θ' phase discovered by Wassermann and Weerts, have reconciled the anomalies in density data. In addition, it should be mentioned that the same considerations apply in explaining the contraction in aluminum-copper alloys after precipitation and growth is complete as shown by Kempf and Hopkins (see p. 266). Although Wassermann and Weerts indicate that the θ' phase transforms to θ at 300°C ., Kempf and Hopkins' data indicate that after 600 hr. at 275°C ., the precipitate is about 60 per cent θ' and 40 per cent θ or normal CuAl_2 . At the lower temperature Kempf and Hopkins' data show that most of the precipitate is in the so-called transition phase θ' . It seems probable, however, that θ' is really a transition phase and not stable at any temperature. Otherwise, a revision in the copper-aluminum equilibrium diagram would be required.

The identity of the precipitating phase in the common age-hardening alloys has been of interest at Hammond Laboratory. It seems possible that an X-ray approach coupled with careful density measurements might generally yield information of the desired character as it has in regard to the aluminum-copper alloys. An investigation directed towards determining the identity of the precipitating phase or phases in duralumin is now in progress here. It involves determining the precipitating phase first in aluminum-magnesium alloys, then in $\text{Al-Mg}_2\text{Si}$ alloys and finally correlating the data for duralumin.

J. T. NORTON,† Cambridge, Mass.—The authors, I think, have made two very valuable contributions in presenting this paper. The first is in the development of a method of showing the very first traces of a precipitate in one of these age-hardening alloys. There can be no question but that this method has now become a very sensitive indicator.

It seems to me the other important contribution is in showing that this system, copper-aluminum, is one of those that show sudden precipitation. Most of the precipitation-hardening alloys fall into two classes, those showing sudden precipitation, which goes to completion in local regions before other regions have started at all, and those showing a gradual and continuous form of precipitation. We have believed that the copper-aluminum system was the outstanding example of this second class,

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which showed gradual precipitation and indicated gradual parameter change. There is much evidence in the literature that has led us to this belief. We now know, as a result of the present work, that this is incorrect and that this system follows many of the others in showing a sudden type of precipitation.

I do not feel, however, that this work has done much to settle the question regarding knots. There is still the anomalous behavior of this particular system, the abnormal change of the resistance and particularly the behavior of the alloy that has been aged at room temperature and then later at a higher temperature, which results in marked softening, followed by hardening again. The original development of the knot theory and the suggestion that it will be possible to distinguish between the formation of knots and formation of actual precipitated particles by lattice-parameter measurements was based on a fallacy, as we now know. It assumed that when the knots were formed the impoverishment of the lattice produced by the copper-rich areas of the knots was very local, so local that it was not detectable by change in parameter, but if precipitates formed, the change in composition of the lattice parameter would be uniformly distributed and show as a change in parameter of the lattice as a whole.

We know that in many of these alloys precipitation does not take place in this way and consequently we could not hope to tell whether the knot theory or precipitation theory was correct.

As a matter of fact, we have no direct way at present by which we can decide between these two possibilities. We know altogether too little about the mechanism of what happens when particles precipitate, or how small particles have to be before they can be called precipitate.

It is difficult to conceive that particles of a definite crystal structure, which they must have if we are to recognize them as definite phases, can form atom by atom. It is also difficult to conceive that particles of a definite crystal structure can spring suddenly fully developed from the solid solution lattice and it seems reasonable to believe there is some intermediate stage; whether we want to call it a knot or beginning of the precipitate particle, seems to me to make very little difference.

To sum up the situation, as I see it, it is rather a waste of time to argue as to whether there are knots or not, until we have some other method, which is not at present available to us, for studying this very difficult stage between the solid solution and precipitate.

R. S. DEAN,* Washington, D. C.—We have been developing for some time the theory of internal surface particularly with respect to minerals. The expression, "internal surface," has been dignified by use in the literature. I have come to the conclusion that precipitation-hardening takes place only subsequent to the formation of internal surface. By "internal surface" I mean a state of affairs which corresponds to that where slip occurs in a metal.

The data around which that argument is built up is a study of magnetic properties. We have found, for example, that with magnetite and other powdered materials, the coercive force was a measure, and a very accurate measure, of internal surface. We have some pretty good data to indicate that this conception can be carried over to cold-work in metals. Some of it is given in Mr. Maier's paper (p. 121). The coercive force changes sharply before the hardness changes in precipitation-hardening alloys. In iron cobalt molybdenum, there are, I think, definite indications that an internal surface is formed and the precipitate, when it comes out, comes out along that internal surface, which, of course, would be an explanation of a thing like Widmanstätten structure where we know that does take place.

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A. PHILLIPS,* New Haven, Conn. (written discussion).—This paper by Messrs. Fink and Smith on the aging characteristics of aluminum-rich copper alloys is important because it presents evidence that precipitation of CuAl_2 takes place in the early stages of low-temperature aging, certainly long before the maximum strengthening effect is attained.

Evidence of this character is particularly interesting to the writer, as he and Dr. Brick¹⁰ after studying the same alloy system stated that "although our data suggests the possibility of an actual precipitation, the evidence is admittedly too meager definitely to establish this point." In a later paper dealing with aluminum-magnesium alloys it was "suggested that certain considerations [referred to in the paper] eliminate the necessity for the concept of 'knot' hardening." Furthermore, Phillips and Brick found that the precipitation reaction in the aluminum-copper alloys in the range 140° to 325° C. yielded a hardness maximum just prior to the time when precipitation, as shown by X-ray methods, was complete. It seems evident that in the binary aluminum-copper system the principal hardening effect is due to precipitation, a view substantiated by the fact that considerably greater hardness is attained at 140° C. than at ordinary temperatures.

The evidence of precipitation in Fink and Smith's Figs. 1 and 2 may be regarded as convincing, although the same evidence presented by less skilled technicians might properly be questioned. The observation that the lattice constant remains unchanged during the early stages of precipitation, as revealed by microscopic examination, is not particularly surprising as it has been demonstrated that X-ray methods are not satisfactory in detecting slight and highly localized changes in concentration of the solid solution lattice. It is reasonable to assume in this case that too little of the parent lattice was affected by precipitation to be picked up by the relatively insensitive diffraction method.

On examining the X-ray data presented by Fink and Smith, the writer was unable to account for the large parameter values reported for the alloy in the two-phase condition, particularly for the alloy heat-treated at 100° C. Phillips and Brick found parameters some 0.0020\AA . larger than that of pure aluminum; Fink and Smith's data include values as high as 4.0634\AA ., or 0.0224\AA . above aluminum. It is interesting to note that the expansion of the lattice beyond the value for aluminum is about twice the contraction produced by the addition of 5 per cent copper. The authors used relatively thin specimens in their work and it is not likely that the large values can be explained on the basis of strain effects resulting from quenching stresses.

The only explanation occurring to the writer is that Fink and Smith measured the extreme edges of the fringes adjacent to the main diffraction lines. Specimens treated in the two-phase region characteristically show areas of asterism beyond the well defined diffraction lines. Measurements of the outer boundaries of the asterism, however, have no significance in the determination of parameter values. The authors made no reference to the large values reported and it will be interesting to learn their views in this regard.

E. E. THUM,† Cleveland, Ohio.—In presenting the paper, the author showed a photomicrograph of the precipitate along certain crystallographic planes and identified those crystallographic planes by squeezing the specimen gently, and then made the statement, which appeared to me to be remarkable (maybe it is not), that slip occurred on planes parallel to those which already had the precipitate.

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¹⁰ A. Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. *Trans. A.I.M.E.* (1934) **111**, 94.

† Editor, *Metal Progress*, American Society for Metals.

As I understand this matter, hardness is resistance to plastic flow, and plastic flow occurs by slip along certain well disposed crystallographic planes. To harden a metal you precipitate some substance along these crystallographic planes and this roughens up the plane so that it resists slip and hardness ensues.

According to such a theory, if precipitation is made to occur on a certain plane, say a 1-1-0 plane, slip ought not to occur along that 1-1-0 plane—yet apparently that is what happens here!

That can be explained perhaps in several ways. Perhaps I have not stated the theory correctly. Perhaps the slip resistance that has been built up by the amount of precipitation that has already occurred is not yet great enough to force subsequent movement, the plastic movement, over into another set of less favorably disposed planes. Maybe the piece on which Messrs. Fink and Smith experimented might have been overaged to the extent that the particles had grown from tiny particles into large particles, and hence lost their maximum power of obstruction; and finally, there is the possibility that my reasoning is faulty.

W. L. FINK.—In regard to the θ' phase, and whether or not it is a stable phase, it might be of interest to mention that we have aged samples at 200° C. for as long as 1000 hr. without appreciably reducing the quantity of θ' phase.

I think one of the rather important points to keep in mind in considering the question of whether the formation of knots is still part of the age-hardening theory is the amount of change in physical properties by the time visible particles appear. Microscopic evidence of precipitation occurs long before there is any large change in properties. In fact, precipitate first occurs when the elongation and yield strength have changed very little, in some cases within experimental error of determining those properties. In other words, if we do have knots that precede the formation of the precipitate particles, they have very little effect on the properties. We certainly do not have to assume the formation of knots in order to explain the changes in properties upon aging. We agree with Professor Norton that we have no way of proving how the embryo submicroscopic crystals form—whether by knots or other type of nuclei. However, this uncertain stage precedes changes in properties and affects age-hardening no more than the method of mobilization affects the strength of an army.

The large parameter values that were observed represent the largest parameters present in the material. The two lines that were shown on the curves do not represent two well defined lines on the X-ray film. There are parameter values all the way in between those two extremes. We are not sure just why we get some values that are so large. It may possibly be due, to a certain extent, to quenching stresses in the material even though the specimens are only 3.2 mm. thick. There may also be stresses set up during the aging process. It is well to keep in mind that the parameter values refer to planes that are nearly parallel to the surface of the specimen, not to any others throughout the material. If we could determine the parameter values for a plane at other angles, they might be quite different. I do not believe that large values of the parameter need cause any great concern. It may be of interest and should be taken into consideration in explaining what is actually happening during the aging process.

In regard to slip on the {111} planes after precipitation has occurred on those planes, I think I am safe in saying that all age-hardenable aluminum alloys behave in this manner even at the point of maximum hardness. There are many {111} planes and perhaps slip does not occur on those particular planes that are well keyed with precipitate particles.

I should like to mention again that the development of the etch by Mr. Keller¹¹ made possible the revealing of these structures in such a definite manner. I should

¹¹ Reference 6.

also like to mention the work of Mr. Walton, who did most of the polishing and etching of these samples. It is not an easy task, since a little too much surface flow during the preparation of the sample, or slightly incorrect time of etching, fails to reveal the precipitate clearly.

R. H. HEYER, * Lafayette, Ind. (written discussion).—This new attack on the problem of the hardening of duraluminum offers some encouragement to instructors who have, in the past several years, attempted to convey the principles of age-hardening to their students. Undoubtedly some teachers of elementary physical metallurgy have stood by the original tenets of simple precipitation-hardening, mainly because the "knots" and many instances of conflicting data and complicated theories were too confusing to impose on the beginning student. It now appears that classroom discussion as well as the hardening particles may again come out in the open. We await the complete story of these researches.

If there is any hesitancy in our reverting to the simple theory, it will not be based on lack of microscopic evidence of early precipitation, but on another experimental fact that has been imposed on the question at frequent intervals in the past. For example, O'Neill, Jackson and Farnham reported the softening effect produced in the early stages of elevated temperature precipitation of previously aged alloys. They used the Meyer hardness analysis instead of ordinary indentation tests to evaluate the softening effect. The writer has been interested in similar applications of the Meyer hardness analysis and wishes to present certain typical data for consideration in the light of the original precipitation-hardening theory as reinstated by Messrs. Fink and Smith.

The following statement by Dr. Rosenhain in his discussion of Gayler and Preston's 1929 paper before the British Institute of Metals has long impressed us as a satisfactory explanation of the conflict of experimental data on precipitation:

"I think that there is one viewpoint about this question of age-hardening which one is apt to forget, and that is that there are two countervailing processes at work. There are possibly more than two, but there are at any rate two: one is the precipitation itself which entails hardening and an increase of electrical resistance by lattice distortion, and the other is the rearrangement of the whole of the crystals, not only the crystals of the precipitated substance but also the rearrangement of the disturbed lattice of the matrix itself, and those make for softening and a decrease of the electrical resistance. I would suggest that one must take into account the fact that with different alloys these two processes will go on at different rates, and consequently the shape of the curves will vary. Therefore, it is not reasonable to attach too much meaning to comparatively slight irregularities of the curves till we can sort out the effects of these two processes which are going on at the same time and producing opposite effects."

The following suggestions may have a further bearing on the reconciliation of the "softening effect" with the principle of true precipitation both at room temperatures and elevated temperatures. As stated in the paper, only a small part of the matrix lattice undergoes dimensional changes simultaneously with the first appreciable change in gross physical properties, and both these changes follow microscopic evidence of precipitation. Assuming, with the authors, that these early changes are due to precipitation of CuAl_2 particles, is it not possible that while the forces tending to cause the formation and precipitation of CuAl_2 may be great enough to effect precipitation in certain favorable locations, yet the other (greater?) forces necessary to rearrange the matrix lattice as a whole, so as to accommodate the foreign phase as best it can, may be lacking?

* Instructor of Metallography, Purdue University.

At room temperature the hardening effect may be due mainly to the presence of precipitated key crystals of CuAl_2 , but partly to the disordered arrangement of the aluminum atoms themselves in the regions along the planes of precipitation. In Figs 5, 6 and 7 we have seen that the distention of the new matrix lattice is greater after aging at room temperature than it is after 160° and 200° C. treatments. The distention after 200° C. is the smallest. May we assume that Dr. Rosenhain's second process, reorganization of the matrix, goes more nearly to completion under the influence of elevated temperatures? While this is undoubtedly a softening process, the softening effect may be more than balanced by new precipitation at certain favorable elevated temperatures.

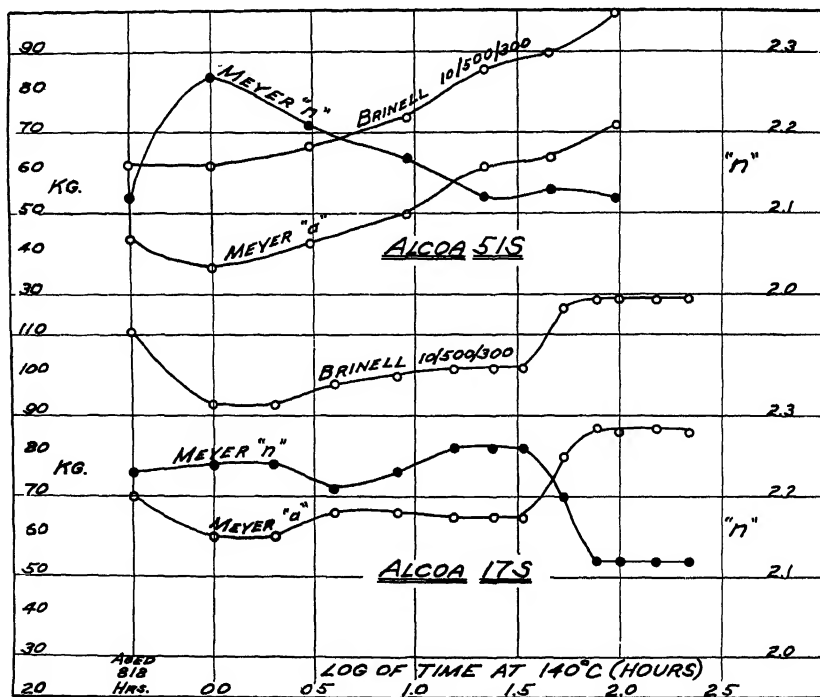


FIG. 8.—HARDNESS CURVES FOR COMMERCIAL ALLOYS.

When an alloy is aged at room temperature and reheated for further precipitation several forces are known to be at work tending to: (1) coarsen those particles already present by continued growth and/or coagulation, (2) reorganize and stabilize, from the structural standpoint, the matrix lattice in the regions where precipitation has occurred, (3) precipitate new hardening particles.

Process 1 may produce either hardening or softening, depending on whether the critical particle size of Merica, Waltenberg and Scott is being approached or surpassed as coarsening proceeds

Process 2 produces softening by reestablishing more planes of easy slip.

Process 3 produces hardening by formation of new crystalline keys, assuming that the temperature and time of treatment are not so great as to produce general overprecipitation.

With these possibilities at hand for a simple binary alloy, we should not be surprised when Meyer hardness curves for commercial alloys show peculiar reversals

and inflections, as illustrated in Fig. 8. In general, curves of this type illustrate the increase in plasticity in the first stages in the heating of pre-aged alloys more effectively than any of the ordinary types of indentation hardness curves, or any of the tensile data we have seen. For the 51S data, for example, the ordinary Brinell 10/500/300 curve gives no indication of the increased plasticity that is unquestionably proved by the drop in Meyer a and remarkable increase in n after one hour reheating time. It would seem that properly executed tensile tests would also bear this out. The writer hopes that Messrs. Fink and Smith will find it possible to include such tests in their comprehensive study.

F. N. RUINES, * Pittsburgh, Pa. (written discussion).—Although it may be unwarranted to attempt to draw general conclusions from the results of a single piece of research, especially when its authors have wisely exhibited restraint in this respect, I am tempted by some of the possibilities suggested by the present metallographic findings. The observation that a visible precipitate occurs along slip planes in the aluminum lattice during the period of increasing hardening may conceivably indicate that plastic deformation of the solid solution crystal is a prerequisite to age-hardening. It is highly improbable that a group of precipitate particles would elect to situate themselves upon a given plane unless that plane differed from its neighbors in some respect. Since the planes selected for precipitation were the slip planes, it seems reasonable to conclude that these individuals were singled out because they had operated in plastic deformation prior to precipitation. Such a view implies that all specimens that exhibit the age-hardening effect must have been subjected to stresses sufficient to induce plastic deformation subsequent to their homogenization, a likely event in view of the observation of Brick, Phillips and Smith that large stresses are set up in aluminum-magnesium alloys upon cooling from the homogenizing temperature even at very slow rates. The well recognized effect of working upon the age-hardening characteristics of duralumin appears to support this view also, in that with increasing amounts of plastic deformation the probable number of active slip planes becomes greater, resulting in the production of a greater abundance and a more general distribution of the possible sites for precipitation with an expected increase in the rate and extent of hardening.

There is nothing new about the concept of the induction of precipitation by plastic deformation, but if it is also true that plastic deformation is necessary to precipitation, it follows that purely elastic strain may not be capable of initiating precipitation. That this may be true has recently been shown by an unpublished work of A. J. Smith, who found no effect of elastic strain upon the rate of age-hardening of aluminum-copper alloys.

The observation of the present authors in a previous investigation¹² that the precipitation in aluminum-magnesium alloys appears to go to completion in certain localized areas before it starts in others is also consistent with the view that precipitation may not be initiated except at widely separated sites such as at the slip planes that have previously operated.

An examination of the photomicrographs of the overaged specimens clearly reveals the presence of large quantities of precipitated material that is not lined up along slip planes. It is possible, however, that these particles started on slip planes of which the traces have been obliterated by the coagulation of the precipitate, but it is likewise possible that they were induced without the benefit of plastic deformation. A careful analysis of data on the effect of plastic deformation on the rate of age-hardening might settle this point. Should it appear that the rate of age-hardening

* Metals Research Laboratory, Carnegie Institute of Technology.

¹² Reference 5.

can be extrapolated to zero at zero deformation, one might safely presume that plastic deformation is necessary to precipitation. Otherwise, plastic deformation may be simply one of the factors controlling the rate of aging.

It is interesting, also, that in spite of the fact that much of the precipitate is concentrated upon a relatively small number of planes, it must, according to our knowledge of the Al-CuAl₂ Widmanstätten figure, occur in the form of thin plates parallel to the cube planes, thereby extending its influence for a distance upon either side of the nuclear slip plane. Thus the precipitate may be expected to interfere with plastic slip upon a number of parallel planes adjacent to the nuclear plane as well as with that upon other families of slip planes.

W. FRAENKEL, Frankfurt a. M., Germany (written discussion*).—In the present investigation it was possible for the authors to render visible by especially careful microscopic work minute particles of precipitate in hardenable aluminum alloys of low copper content during the first stages of aging, while other changes in properties were hardly detectable. In doing so, they have not only produced strong support for the precipitation hypothesis developed by Merica, Waltenberg and Scott, but they have also demonstrated what the classical metallographic method can yield in skilled hands. It would appear particularly interesting to extend the investigation to the magnesium-bearing alloys. It is known that an appreciable increase in the electrical resistivity occurs in these alloys during their rapid spontaneous aging at room temperature, which, aside from other phenomena that I have pointed out (for example, in my publication in *Zeitschrift für Metallkunde*, 22, 1930, 84) causes certain difficulties in explaining the aging by simple precipitation from supersaturated solid solutions. Rendering such minute particles visible would also, in this case, make the assumption probable that very fine dispersoid may produce an increase in electrical resistivity, which up to the present time is only a hypothesis. In regard to alloys free from magnesium as well as the hardenable silver alloys, where these difficulties do not exist, there will no longer be any reason, particularly after the determination by Fink and Smith, to attribute the changes in mechanical properties to anything except the fine precipitate of a second phase. However, I might again point out the special position of the magnesium-bearing alloys, particularly since the possibility of fabricating these from silicon-free aluminum renders untenable the assumption that the compound Mg₂Si plays an important role in these alloys.

W. L. FINK AND D. W. SMITH (written discussion).—Dr. Fraenkel's suggestion that similar work be carried out on an aluminum-copper alloy containing magnesium is pertinent and work on such an alloy is now in progress.

The suggestion made by Dr. Rhines that plastic deformation prior to aging is a necessary prerequisite for aging, was also made in other terms by Dr. R. S. Dean in the oral discussion and by Phillips and Brick in their paper cited in footnote 10. This is an interesting possibility, but the authors have no data to offer in substantiation. It should be remembered that the formation of a particle of precipitate anywhere within the material may favor the formation of other precipitate particles on adjacent portions of the slip planes passing through that point.

* Translated from the German.

Age-hardening of Magnesium-aluminum Alloys

BY A. M. TALBOT,* STUDENT ASSOCIATE A.I.M.E., AND JOHN T. NORTON,†
ASSOCIATE MEMBER

(New York Meeting, February, 1936)

THERE is still considerable controversy as to the exact nature of the mechanism of the age-hardening process, in spite of the many experiments already performed. For this reason, a considerable number of typical systems should be examined in detail and their results correlated. Furthermore, the methods of studying the changes that take place during the progress of this phenomenon should be carefully scrutinized and the different methods applied to the same samples, preferably at the same time. The experiments described in this paper are presented to supply information on one age-hardening system and to show how the various methods of investigation compare in their indication of what has happened. In brief, the progress of aging in magnesium alloys containing about 10 per cent by weight of aluminum at different temperatures was followed by measurements of hardness, electrical resistivity, dilation and lattice parameter, and by microscopic observation.

PREVIOUS WORK

Meissner¹,‡ Archer², and Gann³ have investigated the changes in mechanical properties of magnesium-aluminum alloys during aging and have shown the optimum condition for the age-hardening treatment. Meissner's results are particularly interesting because when replotted so that they represent hardness as a function of aging time, the curves of 125° and 150° C. show two hardness peaks. This result was not confirmed in the present work.

Schmid and Siebel⁴ have reported an investigation that is similar to the present one but it was not published until the present work had

These experiments represent a portion of a thesis presented by A. M. Talbot in fulfilling the requirements of degree of Master of Science at the Massachusetts Institute of Technology. Manuscript received at the office of the Institute, Nov. 23, 1935.

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‡ References are at the end of the paper.

progressed to a considerable extent. These authors compared the changes in mechanical properties during aging with the amount of precipitation as measured by X-rays. A typical set of results is shown in Fig. 1. Where the investigations overlap, they are in general agreement.

Schmid and Seliger⁵ determined the solid solubility of aluminum in magnesium by X-ray methods. They found the maximum solubility

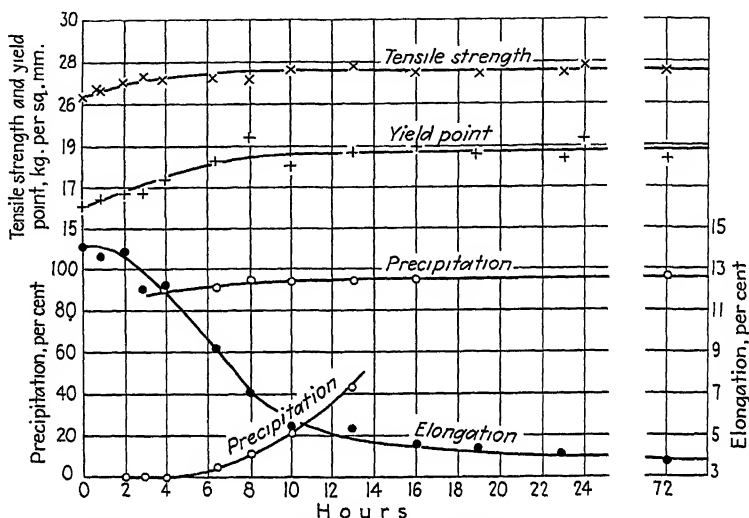


FIG. 1.—RESULTS OF SCHMID AND SIEBEL SHOWING TYPICAL SET OF CURVES.

at the eutectic temperature to be 12.1 per cent, falling to about 2.6 per cent at 150° C. Their data are plotted in Fig. 2.

PREPARATION OF ALLOYS

The alloys were prepared by melting together magnesium and aluminum of high purity and casting in a chill mold. The magnesium was supplied by the Dow Chemical Co. and had the following analysis: Al, 0.02 per cent by weight; Fe, 0.03; Mn, 0.0002; Si, 0.01; Mg (by difference), 99.938. The aluminum was supplied by the Aluminum Company of America and was of the following composition: Si, 0.03 per cent by weight; Cu, 0.01; Fe, 0.06; Al (by difference), 99.90.

The metals were melted in an iron crucible under a flux and bottom-poured into chilled iron molds. A No. 22 flux and No. 13 agent kindly supplied by the Dow Chemical Co. were used.

The ingots as cast were extremely difficult to homogenize. Severe hot working by pressing between steel blocks was necessary if a satis-

factory structure was to be obtained. Apparently diffusion in these alloys is very slow. The samples for X-ray, hardness and microscopic investigation were small slabs about $1\frac{1}{4}$ by $\frac{3}{4}$ by $\frac{3}{8}$ in., and those for resistance and dilation measurements were round rods $\frac{1}{4}$ in. in diameter and 4 in. long.

The determination of aluminum was carried out by the method described by Hillebrand and Lundell⁶. This method gave good checks on test solutions.

EXPERIMENTAL METHODS

The determination of lattice parameter was made by a back-reflection camera using iron radiation. Observations were made on the flat surface of a block. This method is now too well known to require description in detail. No effect of quenching stresses on parameter measurement was observed and the effect shown in the dilation, which might be due to this cause, was small. It is doubtful whether this phenomenon introduces an appreciable

error in the results. The parameters measured were the spacing of the (12.1) and the (11.4) planes and the results were expressed in terms of the percentage of precipitation. When the lines are doubled or broad, representing a range of compositions, this range is represented by a shaded area in the curves. The total change in parameter during aging was about 0.0060 \AA . With sharp lines, the probable error is about $\pm 0.0002 \text{ \AA}$, and this value increases as the lines become broader.

Hardness measurements were made on the reverse side of the block used for the X-ray observations. A Rockwell instrument was used with readings on the B scale. All values reported are averages of at least three readings and the results were more consistent at high readings than at low.

The microscopic observations were made on the same surface used for X-ray work. A dark-field illuminator proved to be most successful for observation of the finely divided precipitate.

All of the above observations were made at room temperature and the aging was interrupted for this purpose. Careful study showed no

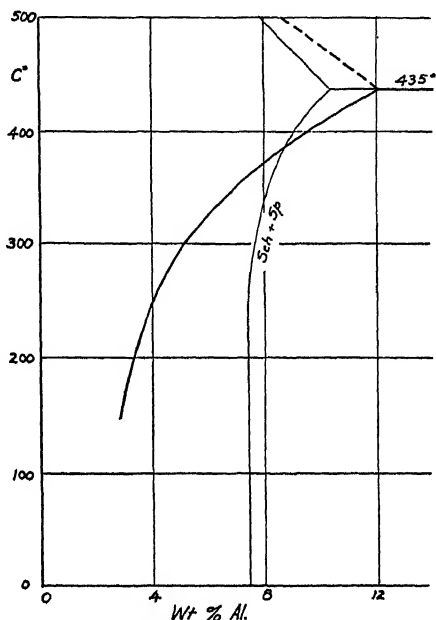


FIG. 2.—SOLUBILITY OF ALUMINUM IN MAGNESIUM AS DETERMINED BY SCHMID AND SELIGER, COMPARED WITH EARLIER RESULTS OF SCHMIDT AND SPITALES.

indication of aging at room temperature after a period of two months, so that this procedure seems justified. The resistivity and dilation measurements, however, were made with the specimen maintained continuously at the aging temperature.

A Kelvin double bridge of conventional design was used for measuring changes in electrical resistivity, which are expressed as percentage changes during aging. The change in resistance of the sample during aging was about 500 microhms and the reading was reproducible to within 5 microhms.

The dilatometer was built according to the specifications of the American Society for Testing Materials⁷. The expanding rod operated a dial gage directly, with sufficient precision. The total change in length was about 80 divisions on the dial.

The aging heat-treatment was carried out under carefully controlled conditions. The solution treatment was for 24 hr. at 415° C. followed by a water quench. The aging temperatures were 100°, 150° and 175° C. and the specimens were maintained in a bath of oil. The oil was heated either electrically or by means of constant boiling mixtures.

EXPERIMENTAL RESULTS

The first series of experiments was performed on alloys containing 9.3 and 10.6 per cent of aluminum by weight. The samples were aged at 100°, 150° and 175° C. and observations of hardness and parameter change were made. These experiments indicated that no parameter change accompanied the very slight hardening at 100° C. and that the beginning of precipitation as shown by changing parameter was delayed as compared with the hardness increase at 150° and 175° C. The microscope, however, showed precipitation at the higher temperatures before a change in parameter was observable, so that the second series of experiments was made.

The latter experiments involved a determination of electrical resistivity and of change in length as well as an observation of the microstructure during aging in addition to the hardness and X-ray tests. A new alloy was prepared, which had a composition of 9.6 per cent Al by weight. The solution heat-treatment was 24 hr. at 415° C. as before and the aging temperatures were 100°, 150° and 175° C. Only the results on this alloy are reported here. Tables 1 to 10 give the results obtained at these aging temperatures and they are combined graphically in curves of Figs. 3 and 4.

DISCUSSION OF RESULTS

The results of this series of experiments show clearly that the age-hardening of these alloys is the result of precipitation. Figs. 3 and 4

TABLE 1.—*Hardness and X-ray Data on Alloy Containing 9.6 Per Cent Aluminum Aged at 100° C.*

Aging Time, Hr.	Hardness, Rockwell B	Precipitation, Per Cent	Appearance of Lines
0	— 8	0	Sharp
48	— 9	0	Sharp
96	—12	0	Sharp
144	— 9	0	Sharp
212	— 6	0	

TABLE 2.—*Dilation of Alloy Containing 9.6 Per Cent Aluminum Aged at 100° C.*

Aging Time, Hr.	Increase in Length, 0.0001 In. in 4 In.	Aging Time, Hr.	Increase in Length, 0.0001 In. in 4 In.
0	0 0	94.0	—0.5
22.5	0 0	120 0	—0 7
46 5	—0.1	142.5	—0.4
70.5	—0.1	190.5	—0.3
		214 5	—0.3

TABLE 3.—*Change in Resistivity of Alloy Containing 9.6 Per Cent Aluminum Aged at 100° C.*

Aging Time, Hr.	Resistivity, Per Cent of Original	Aging Time, Hr.	Resistivity, Per Cent of Original
0	100	113.0	99.6
4.5	99.8	137.0	99.6
16.5	99.8	161 0	99.4
42.5	99.8	185.0	99.4
89.0	99.6	233.0	99.4

TABLE 4.—*Hardness and X-ray Data on Alloy Containing 9.6 Per Cent Aluminum Aged at 150° C.*

Aging Time, Hr.	Hardness, Rockwell B	Precipitation, Per Cent	Appearance of X-ray Lines
0	5	0	Sharp
0.5	4		
1	6		
2	9		
5	12	0	Sharp
10	16	0	Sharp
15	24		
25	38	5- 95	Sharp dual
50	53	18- 97	Slightly diffuse
100	56	52-100	Very diffuse
150	56	65-100	Very diffuse
200	57	72-100	Diffuse

TABLE 5.—*Dilation of Alloy Containing 9.6 Per Cent Aluminum Aged at 150° C.*

Aging Time, Hr.	Increase in Length, 0 0001 In. in 4 In.	Aging Time, Hr.	Increase in Length, 0 0001 In. in 4 In.
0	0	64 0	59.0
2.0	0 1	79 0	65 8
4.0	1 0	85 0	67.3
6.0	1.0	100.0	72 3
10 0	1 9	128.0	77 7
15.5	5.7	148.0	81 0
23 0	14.9	166.0	82 5
25.0	18.0	190 0	84 0
50 5	48 2		

TABLE 6.—*Change in Resistivity of Alloy Containing 9.6 Per Cent Aluminum Aged at 150° C.*

Aging Time, Hr.	Resistivity, Per Cent of Original	Aging Time, Hr.	Resistivity, Per Cent of Original
0	100	84.0	77.9
1.0	99 9	92 0	76.3
3.0	99 7	108 0	74.5
7.0	99.4	119 5	73.7
16.0	97.4	133 0	23.2
20.0	96.1	145 0	72.1
24.5	94.6	157 0	71.6
37 0	89.2	168 0	70.7
50 0	85.2	183.0	70.1
63.0	81.9		

TABLE 7.—*Hardness and X-ray Data on Alloy Containing 9.6 Per Cent Aluminum Aged at 175° C.*

Aging Time, Hr.	Hardness, Rockwell B	Precipitation, Per Cent	Appearance of X-ray Lines
0	— 2	0	Sharp
0 5	+ 7	0	Sharp
1	12	0	Sharp
3	14	0	Sharp
5	25	0—90	Sharp dual
8	44	2—93	Sharp dual
10	46	5—98	Sharp dual
15	51	10—100	Diffuse dual
25	54	20—100	Very diffuse
50	53	60—100	Very diffuse
100	55	80—100	Diffuse
150	51	98	Sharp
200	48	100	Sharp

indicate that the values of hardness, resistivity and change in volume vary in a regular and continuous fashion with the time of aging and that

TABLE 8.—*Dilation of Alloy Containing 9.6 Per Cent Aluminum Aged at 175° C.*

Aging Time, Hr.	Increase in Length, 0.0001 in. in 4 in.	Aging Time, Hr.	Increase in Length, 0.0001 in. in 4 in.
0.0	0 0	25.0	62 5
0 1	-0 9	35 0	66 2
0.2	-1.7	52 0	71.2
3 0	-1.8	61 0	73.0
4.5	+0.1	70.0	73 8
7.0	10.0	84.0	78.0
9 0	23.0	93 0	80 0
10.0	29.1	123 0	82.0
14.0	46.5	148 0	82.5
21.3	59.3		

no significant maxima or minima of the curves appear. At 100° C., practically no changes occur but at 150° and 175° C. full hardening

TABLE 9.—*Change in Resistivity of Alloy Containing 9.6 Per Cent Aluminum Aged at 175° C.*

Aging Time, Hr.	Resistivity, Per Cent of Original	Aging Time, Hr.	Resistivity, Per Cent of Original
0		65.0	70.0
1.0	99.5	89.0	68.7
2.5	99.0	100.0	68.3
5.5	97.0	112.5	67.7
17.0	82.9	149 0	66.1
20.0	80.5	173.0	66.3
25 5	77.7	198.0	66 1
42.5	71 8		

TABLE 10.—*Beginning of Visible Precipitation in Alloy Containing 9.6 Per Cent Aluminum*

AGING TEMPERATURE, DEG. C.	AGING TIME, HR.
20	None at 200 hr.
100	None at 200 hr.
150	1.5
175	0.5

is obtained. The rate of change of these various properties can be accounted for by the simple precipitation theory. The dilation of the sample shows a small negative value during the early stages but this is

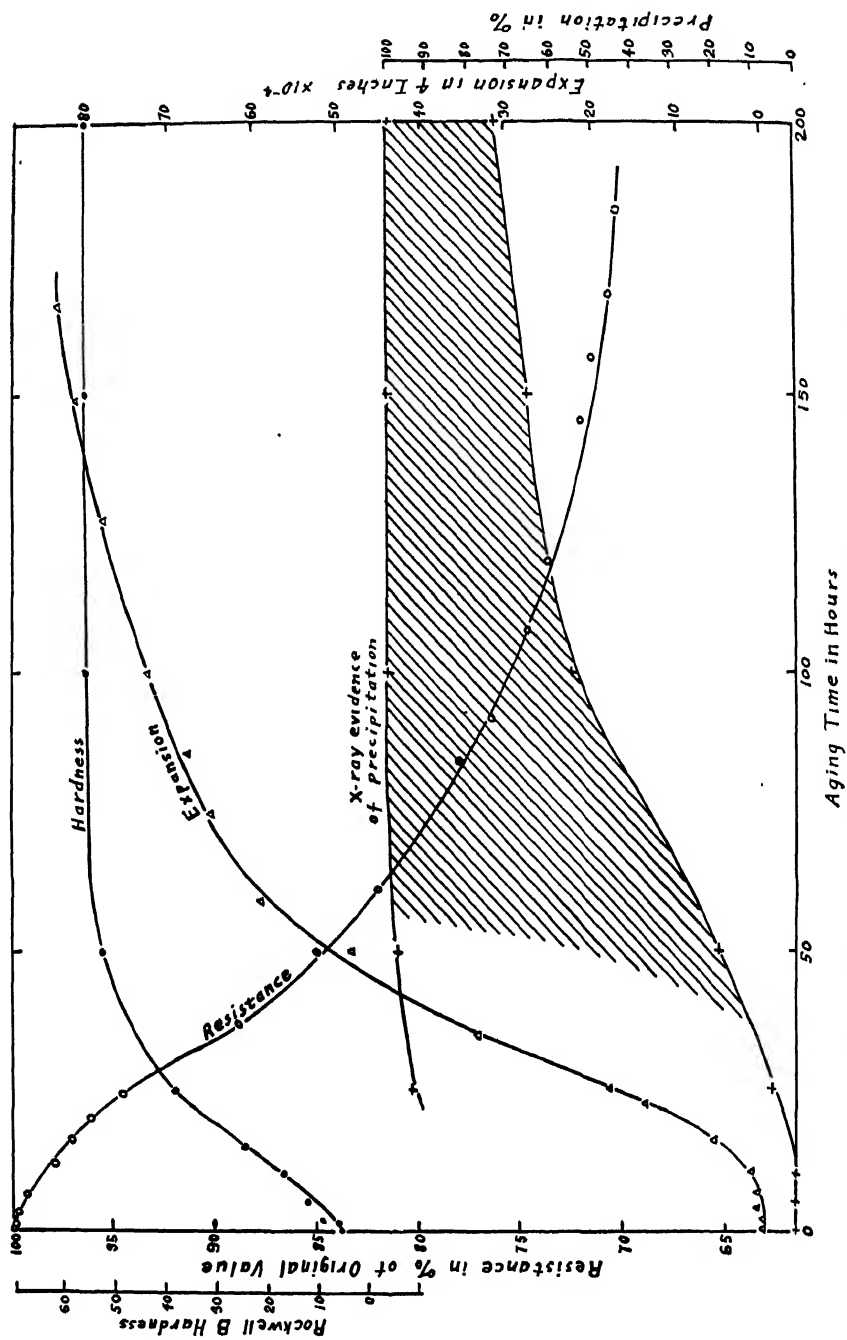


Fig. 3.—RESULTS ON ALLOY CONTAINING 9.6 PER CENT AL AGED AT 150° C.

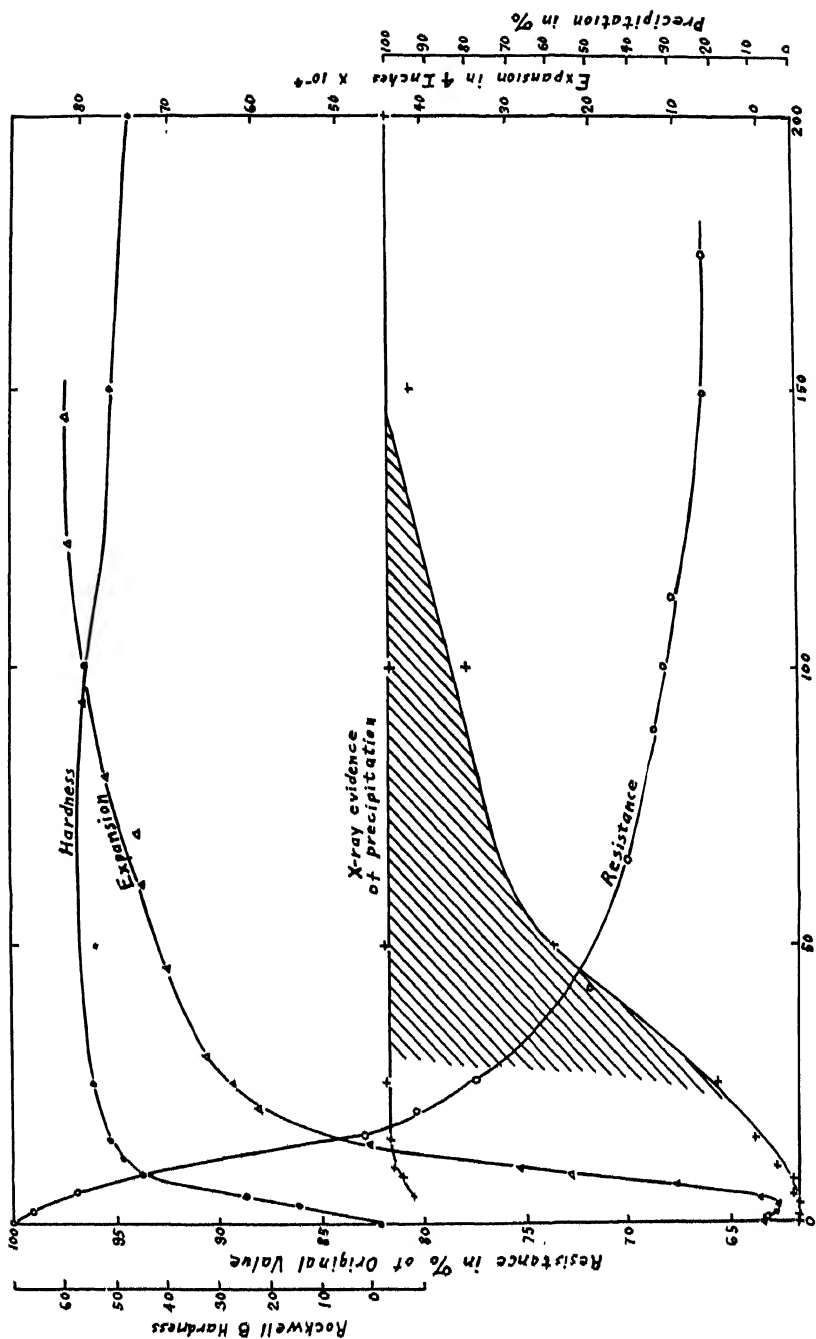


Fig. 4.—RESULTS ON ALLOY CONTAINING 9.6 PER CENT AL AGED AT 175° C.

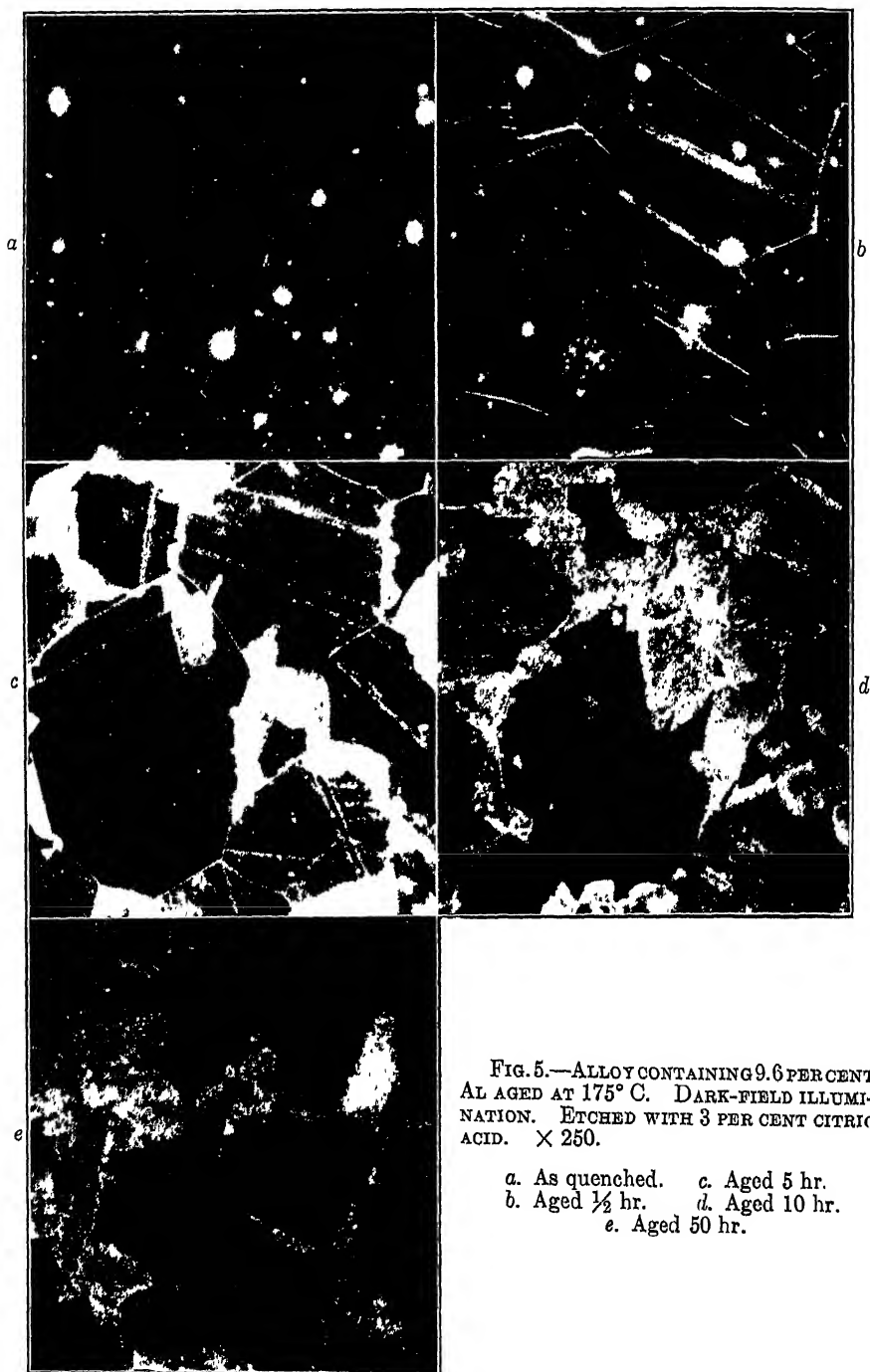


FIG. 5.—ALLOY CONTAINING 9.6 PERCENT AL AGED AT 175° C. DARK-FIELD ILLUMINATION. ETCHED WITH 3 PER CENT CITRIC ACID. $\times 250$.

- a. As quenched. c. Aged 5 hr.
b. Aged $\frac{1}{2}$ hr. d. Aged 10 hr.
e. Aged 50 hr.

believed to be due to the relief of quenching strains in the specimen at the aging temperature. The effect is very small, hardly more than the experimental error.

The changes in microstructure during aging as shown in Fig. 5 indicate plainly the nature of the precipitation process and emphasize

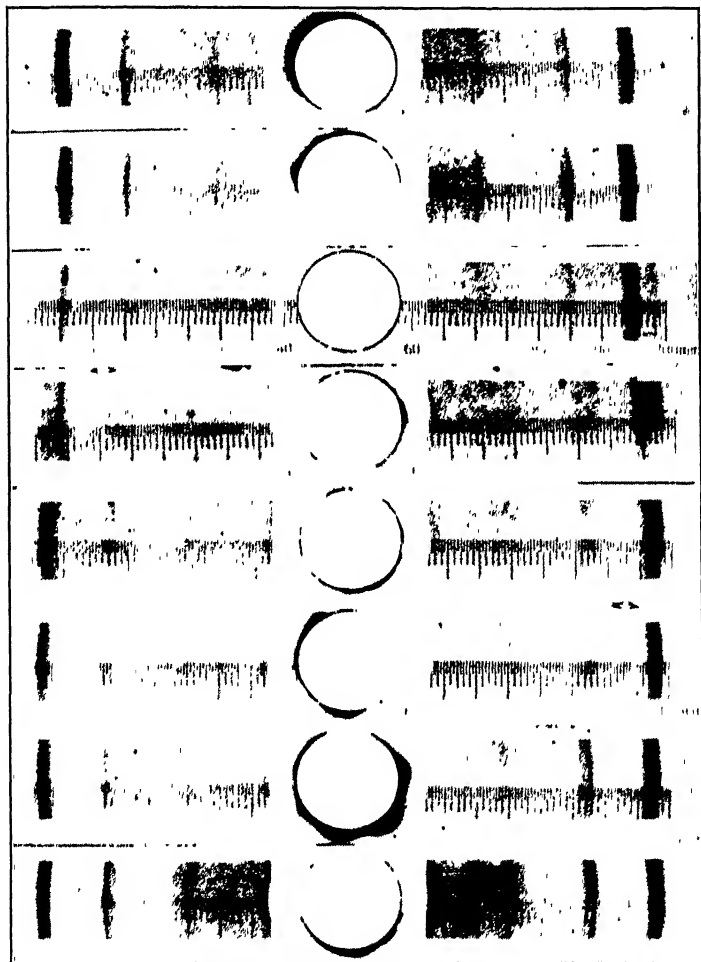


FIG. 6.—CHANGE IN DIFFRACTION PATTERN AT THE 9.6 PER CENT AL ALLOY DURING AGING AT 175° C.

the fact that it does not occur uniformly throughout the grains. This fact is also inferred from the appearance of the X-ray patterns, one set of which appears in Fig. 6. In some systems, the X-ray lines remain sharp and move continuously from the position of the supersaturated

alloy to that of the completely precipitated alloy. This case, however, is quite different. The first effect noted is the appearance of a second set of lines in the position of the completely precipitated solid solution. At this time, both sets are sharp and the microstructure indicates a considerable precipitation at grain boundaries. Apparently this precipitation, once started, goes to completion.

Upon further aging, the second set of lines becomes more intense and the space between the two sets gradually begins to fill in. At this point the microstructure shows the beginning of precipitation in the interior of the grains. Further progress of the aging is marked by a complete disappearance of the first set of lines and a strengthening and sharpening of the second until the solid solution becomes again perfectly uniform in composition. Thus what at first sight seemed a delay in the parameter change in comparison with the hardness change, in other words a pre-precipitation effect, is really due to the fact that the X-ray method is not sufficiently sensitive to detect a composition change in small local regions. In systems that behave in this way, the X-ray method is unsuited for the observation of the beginning of precipitation. It is satisfactory, however, for indicating the completion of this process.

The appearance of massive precipitate at the grain boundaries and finely dispersed precipitate in the centers of the grains suggests that the samples were not homogeneous to start with, in spite of the previous mechanical and thermal treatment, there being a higher aluminum content near the grain surfaces. To test this point, a sample of the same composition was given a solution heat-treatment for 140 hr. instead of the usual 24 hr. and examined in the same way. The results were practically identical but the small differences suggested that with a more completely homogenized alloy the precipitation would be more uniform. It is hoped to repeat some of these experiments with fine powders and with large single crystals, which would eliminate the grain-boundary effect. Another indication of the uneven nature of the precipitation process is the action of the dilatometer while the length of the specimen is increasing rapidly. The pointer of the dial gage has a definitely irregular motion and at times may actually go backward one or two divisions and then take up its forward progress again. This is further evidence that precipitation may go to completion rapidly in local regions.

The behavior of this alloy shows no evidence of pre-precipitation or knot hardening. This idea was originally presented⁸ in order to explain certain anomalies in the resistivity, dilation and lattice parameter during the normal hardness increase. In this particular case, the only anomaly appeared to be that of the lattice parameter change but the microstructure satisfactorily explains this point.

CONCLUSIONS

Conclusions to be drawn from these experiments are as follows:

1. The age-hardening of the magnesium alloys containing about 10 per cent aluminum by weight is due essentially to the precipitation of a second phase from a supersaturated solid solution.
2. The precipitation takes place very unevenly and may go to completion in one region before a neighboring region has started.
3. There is no abnormal behavior of the properties measured that indicates the presence of any sort of pre-precipitation hardening phenomena.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to Mr. F. L. Reynolds and others of the Dow Chemical Co. for their many kindnesses during the course of this investigation. They also desire to express their appreciation of the assistance supplied by Mr. M. Cohen and Mr. T. E. Graves.

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DISCUSSION

(P. N. Rhines presiding)

L. W. KEMPF,* Cleveland, Ohio (written discussion).—I have a feeling—this refers just as much[†] to the preceding paper on the program[†] as to this one—that perhaps we have the necessity, as often occurs in discussions of this kind, for definition of terms. We are apt not to be talking about the same things although we are using the same words.

The process of precipitation or the breakdown of supersaturated solid solutions with the formation of one or more new crystalline phases can be followed by a number

* Aluminum Research Laboratories, Aluminum Company of America.

† W. L. Fink and D. W. Smith: Page 284, this volume.

of different means. The time at a fixed temperature required to attain any specific degree of precipitation varies greatly with the means being used for the detection of precipitation. Probably there are many factors that enter into the hardening effects or changes in mechanical properties, tensile strength, yield strength, hardness and elongation. I believe this is quite evident from the shape of a hardening curve. A general hardening curve depicts an increase to a maximum, followed by a decrease, in hardness with time at a constant temperature. Usually the maximum hardness, again at a constant temperature, is reached long before the maxima or minima in the other physical properties are attained. With such a sequence of events, there is a certain range within which the same hardness will be attained after two widely differing periods of time during the process of precipitation. Undoubtedly the degree of influence exercised by the various factors producing a specific hardness varies greatly between the two time periods that produce identical hardness values.

It is suggested that changes in the physical properties, lattice parameter, electrical resistivity, density, etc., may be the resultants of fewer factors than those which are operative in bringing about changes in mechanical properties, and may therefore be the better indicators, within their sensitivity limits, of the relative quantities of stable and unstable phases present at any specific time.

This paper and the preceding one, by Fink and Smith, present data demonstrating by means of excellent metallographic techniques that lattice-parameter determinations are insufficiently sensitive to indicate the beginning of precipitation. They are, however, probably quite satisfactory for indicating the end point of the reaction. In this connection it is interesting to note in Fig. 4 that the changes in density, resistivity and lattice parameter, produced presumably by precipitation, are completed in substantially the same time. The hardness, however, passes through a maximum considerably earlier in the process. In view of these data it is perhaps not too presumptuous to assume that in this alloy it is only after about 150 hr. at 175° C. that substantial equilibrium is reached between the aluminum-magnesium solid solution stable at this temperature and the newly formed precipitate phase. In other words, it is only after about 150 hr. under these conditions that precipitation is complete. It would appear, therefore, inasmuch as maximum hardness is attained long before precipitation, according to our implied definition, is complete, that the hardening effect must be due to other factors in addition to the presence of discrete crystalline particles of the new phase dispersed in the solid solution.

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Equilibrium Relations in Aluminum-magnesium Silicide Alloys Containing Excess Magnesium

BY F. KELLER* and C. M. CRAIGHEAD*

(New York Meeting, February, 1936)

ALUMINUM alloys containing magnesium and silicon are susceptible to strengthening and hardening by suitable heat-treatments, and they constitute a class of alloys of considerable commercial importance. Generally, they contain these two elements in the proportions required for the formation of the intermetallic compound Mg_2Si , or an excess of silicon; no commercial wrought alloys are made with an appreciable excess of magnesium. The reason for not having excess magnesium is obvious from the results given in this paper, since it is shown that excess magnesium results in a proportional decrease in the solubility of Mg_2Si .

This is the eighteenth[†] of a series of papers from the Aluminum Research Laboratories dealing with the equilibrium relations in aluminum-alloy systems; most of the previous publications concerned binary aluminum-alloy systems; this is the fourth of a group pertaining to ternary aluminum-alloy systems. The work on this system was completed in 1930, but the results were not published because of the pressure of other work.

Hanson and Gaylor², in 1921, presented the results of an extensive investigation of the aluminum-magnesium-silicon system. Their results indicated that an excess of magnesium over the amount required to form the compound Mg_2Si caused a noticeable decrease in the solid solubility of Mg_2Si in aluminum. A more recent investigation³ in these laboratories showed that the solid solubility of Mg_2Si in aluminum was 1.85 per cent at 595° C. and decreased to 0.30 per cent at 300° C. The results of the latter investigation were used as the basis for the present work.

THE PRESENT INVESTIGATION

In the present investigation, a study was made of the effect of various amounts of excess magnesium upon the solid solubility of Mg_2Si in

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† References are at the end of the paper.

aluminum. The alloys employed in this study are in the aluminum corner of the aluminum-magnesium-silicon system, on the magnesium side of the quasi-binary Al-Mg₂Si line. Since these alloys were all readily workable, the samples for the solubility determinations were made up in the form of sheet. Two obvious advantages are to be gained from the use of such wrought specimens, as compared with cast specimens: (1) the alloys are more nearly homogeneous in composition and (2) equilibrium may be approached with a much shorter heating period.

Materials Used.—High-purity aluminum, similar to that employed in other investigations in these laboratories, was used⁴. The silicon and magnesium were also of high purity; the latter was vacuum-distilled metal. The analyses of these metals are given in Table 1.

TABLE 1.—*Analyses of Metals Used in This Investigation*

Metal	Si	Fe	Cu	Mn	Mg	Cr	V	Al	Ti
Aluminum	0.005	0.008	0.006					99.981	
Silicon	99.41	0.29	0.01	0.02	0.01	0.05	0.01	0.15	0.05
Magnesium ^a					99.98			0.01	

^a The magnesium contained 0.01 per cent of group II metals.

Preparation of the Alloys.—Master alloys were prepared by adding predetermined amounts of the silicon and magnesium, in the ratio to form Mg₂Si, to the high-purity aluminum which had been melted in an electric furnace. The compositions of these alloys were as follows:

TABLE 2.—*Analyses of Magnesium Silicide Master Alloys Used in Preparing Ingots*

Alloy No.	Composition, Per Cent				
	Mg	Si	Fe	Cu	Mn
Y2468	0.11	0.07	0.01	0.01	0.00
M9525	0.15	0.10	0.03	0.01	0.00
9526	0.27	0.21	0.03	0.01	0.00
9527	0.52	0.43	0.03	0.01	0.00
9528	0.74	0.56	0.03	0.01	0.00

The master alloys were cast in the form of notched bar; they were subsequently remelted in charges of approximately 600 grams with sufficient added magnesium to produce an alloy of the desired composition. The various charges were cast in a small graphite ingot mold, making ingots $\frac{3}{4}$ by $3\frac{1}{2}$ by 5 in. in dimension. The ingots were heated

12 hr. at 925° F. and hot-rolled at 850° F. to $\frac{1}{4}$ in. The $\frac{1}{4}$ -in. slabs were annealed at 625° F. for 5 hr., cold-rolled to 0.125 in., annealed as before and finally cold-rolled to 14-gage sheet. The analyses of the 14-gage (0.064-in.) sheet samples used in this investigation are given in Table 3.

TABLE 3.—*Analyses of Wrought Alloys Used in This Investigation*

Specimen No.	Composition, Per Cent			
	Si	Mg	Mg ₂ Si, Calculated	Excess Mg, Calculated
Y-2565	0.05	0.39	0.14	0.30
2566	0.05	0.64	0.14	0.55
2567	0.05	0.89	0.14	0.80
2568	0.05	1.16	0.14	1.07
2569	0.05	1.44	0.14	1.35
2570	0.05	1.70	0.14	1.61
2571	0.05	1.95	0.14	1.86
2572	0.05	2.22	0.14	2.13
2573	0.05	2.49	0.14	2.40
M-9532	0.09	0.46	0.25	0.30
9539	0.09	0.68	0.25	0.52
9546	0.09	1.22	0.25	1.06
9553	0.09	2.22	0.25	2.06
9540	0.18	0.90	0.49	0.59
9554	0.19	2.41	0.52	2.08
9533	0.21	0.69	0.57	0.33
9547	0.21	1.39	0.57	1.03
Y-2574	0.26	1.04	0.71	0.59
M-9548	0.39	1.75	1.07	1.07
9541	0.40	1.28	1.09	0.59
9534	0.44	1.03	1.20	0.27
9535	0.53	1.26	1.45	0.34

Heat-treatment of Specimens.—In the first attempts to heat-treat the sheet specimens for long periods at elevated temperatures to produce equilibrium, it was noted that the sheet became blackened and badly blistered. The cause of the discoloration and blistering was traced to the action of water vapor in the furnace atmosphere. In order to avoid the discoloration and blistering resulting from this action, a dry-air furnace was constructed for the heat-treatment of the specimens. The procedure consisted essentially in drying air by passing it through sulfuric acid and activated alumina towers. The dried air was first passed through a glass preheating coil in the furnace and then to a glass heat-treating chamber inside a large cylindrical block of aluminum. The front of the aluminum block was closed by means of an aluminum plug, which contained a small hole for the thermocouple and another for the

exit tube for the air. The air leaving the furnace chamber was passed through a bubble tube in order to maintain a positive air pressure. By keeping an atmosphere of dry air in the furnace, the entrance of water vapor was largely prevented. With this arrangement, the sheet samples could be heat-treated at the high temperatures without developing signs of blistering or other decomposition.

Specimens of a suitable size for microscopic examination were placed in the heat-treating chamber and held for 144 hr. at 535° C., after which the first set was removed and quenched. The temperature of the specimens was then lowered to 500° C. in 24 hr., held at 500° C. for 24 hr. and another set was removed and quenched. Then the temperature was lowered to 470° C. in 24 hr., held at 470° C. for 48 hr. and the third set of specimens was removed and quenched. Again the temperature was lowered in 24 hr. to 440° C., held at 440° C. for 72 hr. and the fourth set of specimens removed and quenched. Finally, the temperature was lowered to 400° C. in 24 hr., held 96 hr. at 400° C. and the last set of specimens was removed and quenched.

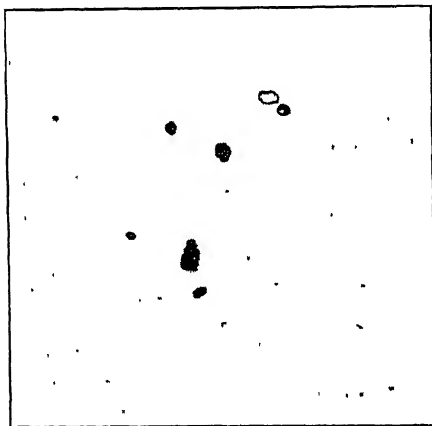


FIG. 1.—PARTICLES OF Mg_2Si IN ALLOY CONTAINING 0.09 PER CENT Si AND 2.22 PER CENT Mg (0.25 Mg_2Si 2.06 PER CENT EXCESS Mg) AFTER SAMPLE HAD BEEN ANNEALED 144 HOURS AT 535° C. AND QUENCHED. UNETCHED. $\times 500$.

No attempt was made to obtain equilibrium with a rising temperature. In view of the prolonged times employed with the wrought specimens, it was felt that equilib-

rium was closely approached with these treatments.

Microscopic Examination.—The solid solubility relations were determined by means of microscopic examination. Therefore, metallographic specimens of the quenched sheet samples were made, in composite form. In each composite specimen, the individual samples of a given magnesium silicide content were arranged in order of increasing magnesium content; thus it was possible to determine readily the composition in which the first particles of Mg_2Si were present. In general, the specimens were not etched, since the etching reagents commonly employed attacked the magnesium silicide particles severely; the pale iridescent blue color of freshly polished Mg_2Si and the prismatic crystal form were used as distinguishing characteristics. In a few instances, particles of constituent were noted that could not be identified definitely as the Mg_2Si compound. Where there was any doubt regarding the identity of such particles in the microstructure, Mg_2Si was said to be absent,

TABLE 4.—*Results of Microscopic Examination*

Specimen No.	Calculated Composition, Per Cent		Microscopic Examination	
	Mg ₂ Si	Excess Mg	Mg ₂ Si Present	Mg ₂ Si Absent
SPECIMENS HEATED 144 HR. AT 535° C. AND QUENCHED				
Y-2565	0.14	0.30		*
2566	0.14	0.55		*
2567	0.14	0.80		*
2568	0.14	1.07		*
2569	0.14	1.35		*
2570	0.14	1.61		*
2571	0.14	1.86		*
2572	0.14	2.13		*
2573	0.14	2.40	*	
M-9532	0.25	0.30		*
9539	0.25	0.52		*
9546	0.25	1.06		*
9553	0.25	2.06	*	
9540	0.49	0.59		*
9554	0.52	2.08	*	
9533	0.57	0.33		*
9547	0.57	1.03	*	
Y-2574	0.71	0.59		*
M-9548	1.07	1.07	*	
9541	1.09	0.59	*	
9534	1.20	0.27	*	
9535	1.45	0.34	*	

SPECIMENS HEATED 144 HR. AT 535° C., COOLED TO 500° C. IN 24 HR., HELD 24 HR.
AT 500° C. AND QUENCHED

Y-2565	0.14	0.30		*
2566	0.14	0.55		*
2567	0.14	0.80		*
2568	0.14	1.07		*
2569	0.14	1.35		*
2570	0.14	1.61		*
2571	0.14	1.86		*
2572	0.14	2.13		*
2573	0.14	2.40	*	
M-9532	0.25	0.30		*
9539	0.25	0.52		*
9546	0.25	1.06		*
9553	0.25	2.06	*	
9540	0.49	0.59		*
9554	0.52	2.08	*	
9533	0.57	0.33		*
9547	0.57	1.03	*	
Y-2574	0.71	0.59	*	

TABLE 4.—(Continued)

Specimen No.	Calculated Composition, Per Cent		Microscopic Examination	
	Mg ₂ Si	Excess Mg	Mg ₂ Si Present	Mg ₂ Si Absent
SPECIMENS HEATED 144 HR. AT 535° C., COOLED TO 500° C. IN 24 HR., HELD 24 HR. AT 500° C., COOLED TO 470° C. IN 24 HR., HELD 48 HR. AT 470° C. AND QUENCHED				
Y-2565	0.14	0.30		*
2566	0.14	0.55		*
2567	0.14	0.80		*
2568	0.14	1.07		*
2569	0.14	1.35	*	
2570	0.14	1.61	*	
2571	0.14	1.86	*	
2572	0.14	2.13	*	
2573	0.14	2.40	*	
M-9532	0.25	0.30		*
9539	0.25	0.52		*
9546	0.25	1.06	*	
9553	0.25	2.06	*	
9540	0.49	0.59	*	
9554	0.52	2.08	*	
9533	0.57	0.33		*
9547	0.57	1.03	*	
2574	0.71	0.59	*	
M-9548	1.07	1.07	*	
9541	1.09	0.59	*	
9534	1.20	0.27	*	
9535	1.45	0.34	*	
SPECIMENS HEATED 144 HR. AT 535° C., COOLED TO 500° C. IN 24 HR., HELD 24 HR. AT 500° C., COOLED TO 470° C. IN 24 HR., HELD 48 HR. AT 470° C., COOLED TO 440° C. IN 24 HR., HELD 72 HR. AT 440° C. AND QUENCHED				
Y-2565	0.14	0.30		*
2566	0.14	0.55		*
2567	0.14	0.80	*	
2568	0.14	1.07	*	
2569	0.14	1.35	*	
M-9532	0.25	0.30		*
9539	0.25	0.52		*
9546	0.25	1.06	*	
9553	0.25	2.06	*	
SPECIMENS HEATED 144 HR. AT 535° C., COOLED TO 500° C. IN 24 HR., HELD 24 HR. AT 500° C., COOLED TO 470° C. IN 24 HR., HELD 48 HR. AT 470° C., COOLED TO 440° C. IN 24 HR., HELD 72 HR. AT 440° C., COOLED TO 400° C. IN 24 HR., HELD 96 HR. AT 400° C. AND QUENCHED				
Y-2565	0.14	0.30		*
2566	0.14	0.55	*	
2567	0.14	0.80	*	
2568	0.14	1.07	*	
2569	0.14	1.35	*	
M-9532	0.25	0.30	*	
9539	0.25	0.52	*	
9546	0.25	1.06	*	
9553	0.25	2.06	*	

The microstructure of an alloy containing 0.25 per cent Mg_2Si and 2.06 per cent excess magnesium is shown in Fig. 1. The particles of Mg_2Si that appear are in excess of the solid solubility. The solubility of Mg_2Si in this specimen was less than 0.25 per cent when the above amount of excess magnesium was present, as compared with a solid solubility of 1.36 per cent when no excess magnesium was present. This serves to illustrate the effect of excess magnesium upon the solid solubility of Mg_2Si in aluminum.

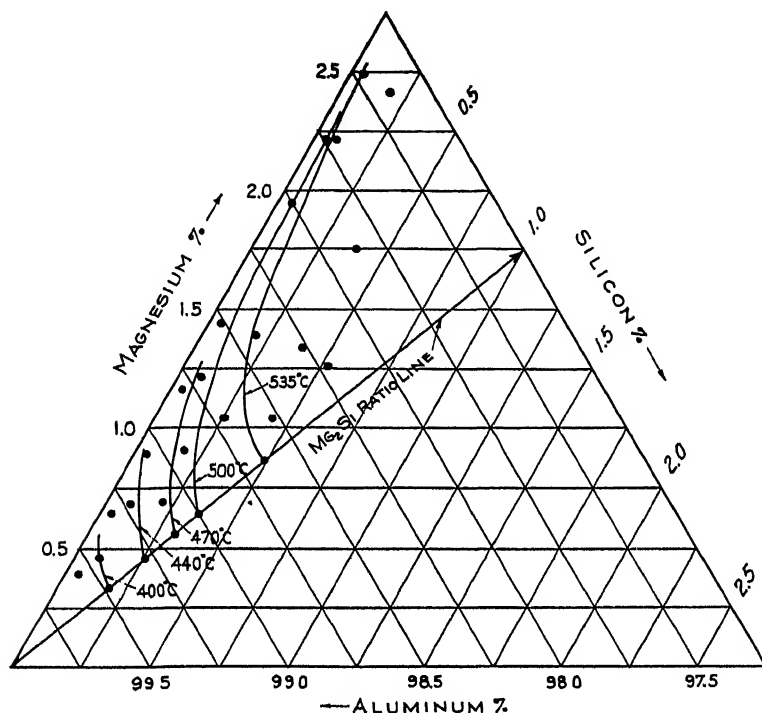


FIG. 2.—RESULTS OBTAINED BY MICROSCOPIC EXAMINATION OF SPECIMENS QUENCHED FROM VARIOUS TEMPERATURES. ISOTHERMS AT EACH TEMPERATURE GIVE SOLID SOLUBILITY VALUES.

Solubility Relations.—The results obtained by microscopic examination of sheet specimens quenched after prolonged heating at 535°, 500°, 470°, 440° and 400° C. are included in Table 4. From these data the solubility isotherms shown in Fig. 2 were plotted. These isotherms show the decrease in solid solubility at a given heat-treating temperature when the amount of magnesium in excess of that required to form Mg_2Si is increased. The solid solubility values plotted on the quasi-binary Al- Mg_2Si line in this diagram were obtained from the results of previous work in these Laboratories³. The curves in Fig. 3 were derived from the results shown in Fig. 2. In this diagram, the curves show the solubility

of Mg_2Si at a given temperature with various amounts of magnesium in excess of the Mg_2Si ratio. The curves shown in Fig. 4 were in turn derived from the results shown in Fig. 3. In this diagram the effect of excess magnesium is shown plotted against temperature. The results include only the temperature range employed for heat-treatment. No values were obtained in the low-temperature range.

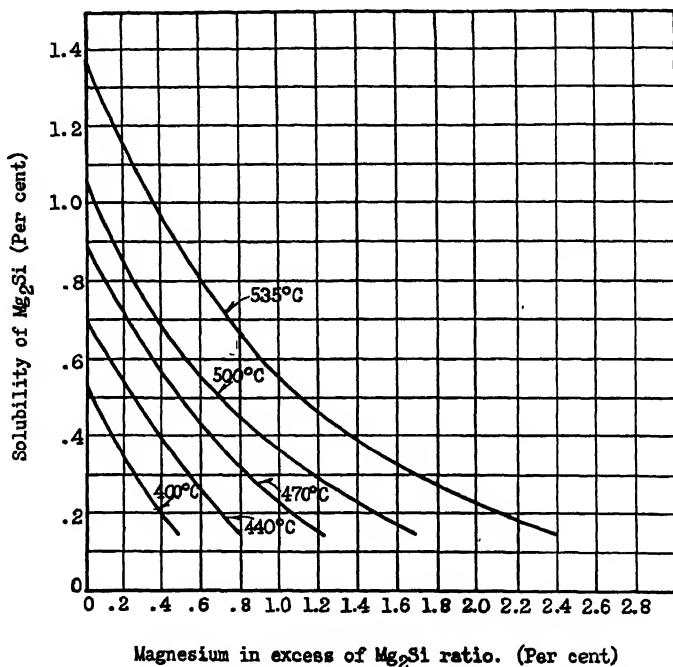


FIG. 3.—SOLUBILITY VALUES PLOTTED AGAINST EXCESS MAGNESIUM CONTENTS. DATA WERE DERIVED FROM CURVES SHOWN IN FIG. 2.

DISCUSSION OF RESULTS

From the results obtained from this investigation, it will be noted that the presence of magnesium in excess of that required to form the compound Mg_2Si results in a proportional decrease in the solid solubility of Mg_2Si in aluminum. This information is of considerable commercial value, since the mechanical properties of alloys of the Mg_2Si type are dependent upon the amount of Mg_2Si that can be dissolved during heat-treatment and precipitated by artificial aging. Thus in these alloys, the presence of any appreciable amount of excess magnesium would result in a lowering of the mechanical properties. For this reason, wrought alloys of Mg_2Si type containing an excess of magnesium over that required to form Mg_2Si are of little commercial importance.

ACKNOWLEDGMENT

The authors desire to express their appreciation to Mr. E. H. Dix, Jr., under whose direction this work was carried out, and to Mr. H. V. Churchill, for the chemical analyses of the alloys.

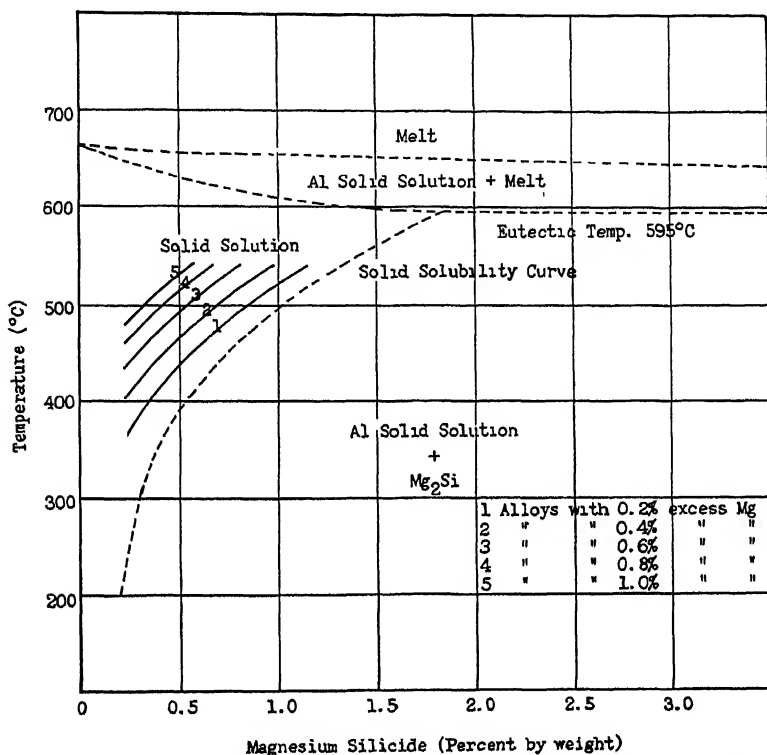


FIG. 4.—SOLUBILITY OF Mg_2Si IN ALLOYS CONTAINING A CONSTANT EXCESS OF MAGNESIUM. VALUES FOR CONSTRUCTION OF CURVES WERE DERIVED FROM RESULTS SHOWN IN FIG. 3.

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4. F. C. Frary: Electrolytic Refining of Aluminum. *Trans. Amer. Electrochem. Soc.* (1925) **47**, 275.

Diffusion of Magnesium and Silicon into Aluminum

BY HERTHA R. FRECHE*

(New York Meeting, February, 1936)

THE diffusion of magnesium and silicon from the core into the high-purity coating of Alclad sheet is important commercially, and led to the use of a duplex product for the study of diffusion by means of spectrographic analysis of successive layers.

It has been found that in the duplex materials the diffusion of magnesium from an undersaturated aluminum-magnesium alloy into its high-purity aluminum coating is approximately of the same order of magnitude as the diffusion of silicon from a saturated aluminum-silicon alloy into its high-purity aluminum coating. However, if magnesium and silicon are both present in the alloy in the ratio of Mg_2Si , they appear to diffuse in the approximate ratio of this compound. Finally, if the alloy contains silicon in excess of the amount required by magnesium silicide, the amount of diffused silicon in the high-purity aluminum coating will also be in excess.

The interdiffusion of metals in the solid state is of both scientific and technical interest, because it is helpful in the study of the alloy structure and in the solution of problems pertaining to the strength and surface condition of the fabricated product.

W. C. Roberts-Austen¹† carried out the first quantitative determination of the coefficient of diffusion of gold into lead. This classical experiment was followed by a series of investigations on the diffusion of metals and nonmetals in iron and steel and in nonferrous metals and alloys. Recently the diffusion of copper in coated strong aluminum alloys was investigated by A. Burkhardt². This appeared to be the first published investigation on the diffusion of metals into aluminum.

The present investigation was the direct result of a technical question in connection with alloy fabrication and is a summary of some preliminary work pertaining to the diffusion of magnesium and silicon into aluminum. The results necessarily will be subject to some variations, since this is the first attempt to evaluate the coefficients of diffusion of magnesium and silicon into aluminum according to this method of procedure. This

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† References are at the end of the paper.

method, however, gives a definite indication of the relative magnitudes of the rates of diffusion of magnesium and silicon into aluminum.

The investigation was carried out on Alclad³ material. The magnesium and silicon in the high-purity alloy core diffused into the high-purity aluminum⁴ coating.

The rates of diffusion of magnesium and silicon from the alloy core into the high-purity aluminum coating were determined from the quantitative spectrographic data obtained from a series of 0.003-in. (0.0076 cm.) deep steps machined in the Alclad coating. In addition, it was also determined by means of quantitative spectrographic analysis how the simultaneous presence of silicon affects the rate of diffusion of magnesium into aluminum: (1) When the magnesium and silicon in the alloy core are present in the ratio of the intermetallic compound Mg_2Si , and (2) when the amount of silicon present in the alloy core is in excess of the amount required by the compound Mg_2Si .

PREPARATION OF SPECIMENS

Electrolytically refined aluminum was used for the preparation of the alloy core and coating. The chemical analysis of the aluminum showed the following impurities: 0.010 Si, 0.010 Fe, 0.005 Cu.

A high-purity aluminum-silicon alloy, which contained only 0.05 per cent iron, and sublimed magnesium were used for the preparation of the alloy cores. The analysis of the various alloys used as cores for the Alclad materials are given in Table 1.

TABLE 1.—*Composition of Alloy Cores of Alclad Specimens*

Specimen No.	Intended Mg_2Si Composition		Weight Per Cent		Atomic Per Cent	
	Weight Per Cent	Molecular Per Cent	Mg	Si	Mg	Si
S10862			1.21		1.340	
S10861				1.95		1.875
S11302	1.80	0.644	1.21	0.63	1.340	0.616
S10860	1.80 + 0.71 per cent excess Si	0.644 + 0.66 atomic per cent excess Si	1.61	1.35	1.285	1.296

Fabrication of Alclad Material.—The alloys were chill-cast in the form of 1-lb. ingots 2 by 9 by 10 cm. In order to prevent diffusion such as would occur during the casting of the alloy melt against the high-purity aluminum liners, for this investigation the high-purity aluminum coating was merely rolled on to both sides of the alloy ingots after proper surface preparation of the metals. The resulting material was rolled down to the form of slab about 12.7 cm. wide and 0.63 cm. thick. The average

coating thickness on either side of the slab corresponded to about 0.063 cm. This value, however, varied within approximately ± 0.005 cm. because of slight irregularities produced during the rolling of the material. The average coating thickness of the samples was determined by means of microscopic measurements.

Preparation and Microstructure of Specimens Used for Diffusion Experiments.—The specimens used

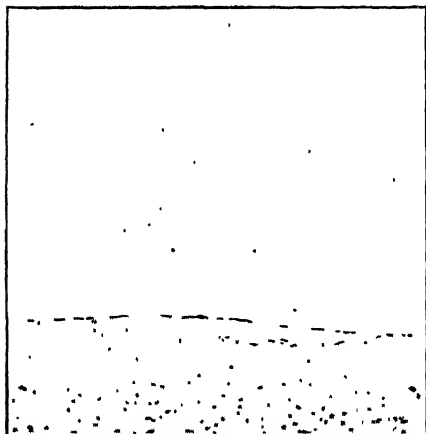


FIG. 1.—ALLOY CORE CONTAINING 1.95 PER CENT SILICON WITH AN ALUMINUM-SILICON SOLID SOLUTION COATING (S16387-A10206). $\times 100$. ETCHED WITH 0.5 PER CENT HF.

Specimen was heat-treated for 48 hr. at 510° C. and quenched. Shows penetration of oxide film into alloy core at grain boundaries and impoverishment of alloy core in silicon particles along interface. Presence of oxide film is undoubtedly due to method of manufacture of miniature ingot.

for the diffusion experiments were cut from sections of the Alclad slabs that appeared to be flat. The cut specimens were 12.7 cm. long, 1.27 cm. wide and 0.63 cm. thick. These strips were heat-treated at 450° and 510° C. for periods of time varying from 36 to 73 hr. and quenched in cold water.

A metallographic specimen was cut from each strip to determine the coating thickness and the character of the bond between the alloy core and coating. Microscopic examination revealed a continuous bond between the alloy core and coating and the presence of traces of oxide film in almost all specimens. The presence of detectable amounts of oxide film in Alclad material is unusual and probably was due to the method of manufacture of the miniature ingots. The amount of

reduction by rolling was not enough to break up any residual film. The film appeared to originate at the bond and to project into the alloy core. In no case did the film enter the high-purity coating. Fig. 1 illustrates a section of the bond between the high-purity aluminum-silicon alloy core containing 1.95 per cent silicon and the high-purity aluminum-silicon solid solution coating (specimen S10861). The oxide film, which apparently originated at the interface between the core and coating, penetrated the aluminum-silicon alloy core. It is also apparent from the photomicrograph that the area adjoining the Alclad coating has been greatly impoverished in silicon particles which diffused into the coating to form a solid solution.

After it had been established by microscopic examination that the bond between the alloy core and coating was satisfactory, except for the slight defects pointed out above, the diffusion specimens were prepared for quantitative spectrographic analysis. This was done by removing the

Alclad coating in steps corresponding to 0.003 in. (0.0076 cm.) on one side of each specimen by careful machining. Each machined specimen had seven steps, excluding the original surface, so that the maximum depth to which each specimen was machined corresponded to 0.021 in. (0.053 cm.). The diagrammatic sketch (Fig. 2) indicates the side view of the machined specimen.

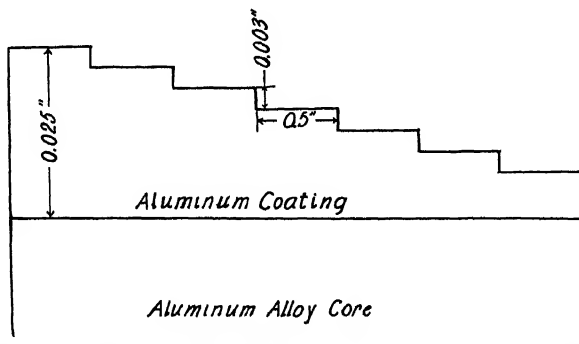


FIG. 2.—SPECIMEN A8447. DIAGRAMMATIC SKETCH ILLUSTRATING APPEARANCE OF SIDE VIEW OF MACHINED ALCLAD SAMPLE.

Several instances were observed where the machined surfaces were extremely rough. For this reason no spectrographic determinations were made on such areas. All machined areas showed more or less surface roughening when examined under the microscope.

QUANTITATIVE SPECTROGRAPHIC ANALYSIS

The magnesium and silicon contents corresponding to the surfaces of the various steps in the Alclad coating were determined under the direc-

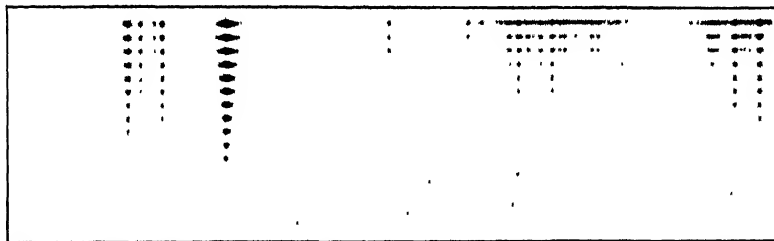


FIG. 3.—SPECIMEN A9494. APPEARANCE OF SPECTRUM USED IN LOGARITHMIC SECTOR PHOTOMETRIC EVALUATION OF MAGNESIUM CONTENT IN ONE STEP OF ALCLAD COATING.

tion of Mr. A. W. Petrey, of these laboratories, by quantitative spectrographic analysis according to the method he developed. The machined surface of the Alclad sample served as one electrode, and a high-purity aluminum rod as the other. The spectrum produced by the spark

between the two electrodes was evaluated by a logarithmic sector photometer. The appearance of such a series of lines, corresponding to

Distance
from In-
terface, Cm.

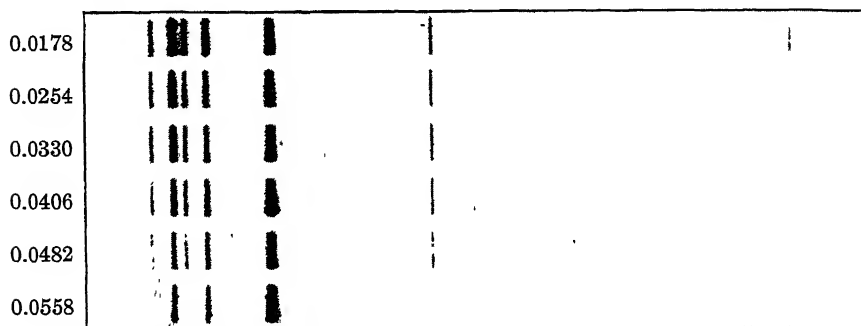


FIG. 4.—SPECIMEN A9493. ILLUSTRATES LINE SPECTRA CORRESPONDING TO SIX SUCCESSIVE STEPS, ACCORDING TO SKETCH IN FIG. 2, IN ALCLAD COATING OF HIGH-PURITY ALUMINUM-MAGNESIUM ALLOY CORE CONTAINING 3 PER CENT MAGNESIUM.

Specimen was heat-treated for 73 hr. at 450° C. and quenched. These spectra were not used for evaluation, but are shown here merely to illustrate decrease of magnesium content from interface to surface.

one step in the coating and produced by this method, is illustrated by Fig. 3. Fig. 4 illustrates the spectra corresponding to six steps in the

Alclad coating of an aluminum-magnesium alloy core which contained 3 per cent magnesium. The specimen was heat-treated at 450° C. for 73 hours.

The accuracy of the quantitative spectrographic determination of magnesium has recently been greatly increased. At the time when these experiments were carried out, a magnesium content of 0.005 per cent could be determined within ± 0.003 per cent and a silicon content of 0.02 within 0.01 per cent.

Results of Spectrographic Analysis.—Since the results obtained from the spectrographic analysis were used as a quantitative measure of the progress of diffusion, it was of great interest to determine the depth of the craters produced by the spark on the machined surfaces in the Alclad coating of the diffusion

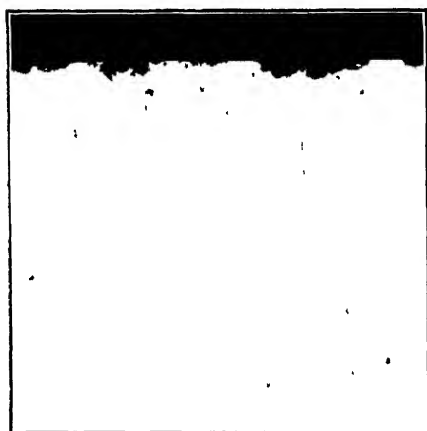


FIG. 5.—SURFACE SECTION OF ALCLAD COATING ON ALUMINUM-MAGNESIUM-SILICON ALLOY CORE CONTAINING 1.16 PER CENT MAGNESIUM AND 1.35 PER CENT SILICON (S17696-A9372). $\times 500$.

Specimen was heat-treated for 73 hr. at 510° C. and quenched. Shows superficial surface roughening produced by spectral spark.

spark on the machined surfaces in the Alclad coating of the diffusion

specimens. Measurements of the depths of these cavities were made by means of an optical micrometer on cross sections taken through the center of the craters. The maximum depth of penetration of the spark into the metal surface varied from 0.0003 to 0.0005 in. (0.0007 to 0.0013 cm.). Fig. 5 illustrates the appearance of such a cross-sectional area. It is apparent that the indentations produced by the spark are extremely shallow, and that the quantitative data, therefore, are representative of the surfaces spectrographed.

The quantitative data corresponding to the series of steps or depths of diffusion in the Alclad coating and the periods of heat-treatment of

TABLE 2.—*Diffusion of Magnesium into Aluminum*

Specimen No.	Thermal Treatment		Distance, x , Cm.	x^2	Conc. of Mg in Al Coating		
					Observed		Calculated, Atomic Per Cent
	Temp., Deg. C.	Time, Hr.			Wt. Per Cent	At. Per Cent	
10862-A	450	48	0.01270	0.0001613	0.40	0.443	0.414
			0.02032	0.0004129	0.30	0.332	0.284
			0.02794	0.0007806	0.20	0.221	0.183
			0.03556	0.0012645	0.10	0.111	0.111
			0.04318	0.0018645	0.01	0.011	0.060
			0.05080	0.0025806	0.005	0.005	0.031

TABLE 3.—*Diffusion of Silicon in Aluminum*

Specimen No.	Thermal Treatment		Solid Solubility of Si in Al at 510° C.		Distance, x, Cm.	Concentration of Si in Al Coating			
	Temp., Deg. C.	Time, Hr.	Weight Per Cent	Atomic Per Cent		Observed		Calculated, Atomic Per Cent	
						Weight Per Cent	Atomic Per Cent		
S10861	510	48	0.83	0.772	0.02286	0.40	0.384	0.298	
					0.03048	0.20	0.192	0.190	
					0.03810	0.08	0.076	0.114	
					0.04572	0.04	0.038	0.065	
					0.05334	0.02	0.019	0.033	
	57				0.01778	1.00 ^a	0.961 ^a		
					0.02540	0.80 ^a	0.769 ^a		
					0.03302	0.60 ^a	0.576 ^a		
					0.04064	0.20	0.192		
					0.04826	0.04	0.038		
					0.05588	0.02	0.019		

^a Because of the presence of free silicon in the coating, these values were not included in the determination of the average coefficient of diffusion of silicon in aluminum.

the diffusion specimens are summarized in Tables 2 to 5. The concentration of the diffused material is expressed in atomic per cent magnesium, silicon, and molecular per cent magnesium silicide and the distance x in centimeters. With the exception of the few discrepancies already

TABLE 4.—*Diffusion of Magnesium and Silicon in Aluminum from an Aluminum-alloy Core Containing an Excess of Magnesium Silicide*

Specimen No.	Thermal Treatment		Solid Solubility in Al at 510° C.		Distance, x , Cm.	Concentration of Mg and Si in Al Coating						Molecular Per Cent Mg_2Si + Excess Atomic Per Cent Si or Mg		
	Temp., Deg. C.	Time, Hr.	Si, Atomic Per Cent	Mg_2Si , Molecular Per Cent		Observed				Calculated, Atomic Per Cent				
						Weight Per Cent		Atomic Per Cent						
						Mg	Si	Mg	Si	Mg	Si			
S11302	510	36	0.772	0.403	0.01524	0.40	0.30	0.443	0.288	0.416	0.349	0.221 Mg_2Si + 0.067 Si		
					0.02286	0.30	0.20	0.332	0.192	0.304	0.236	0.166 Mg_2Si + 0.025 Si		
					0.03048	0.20	0.15	0.221	0.144	0.211	0.150	0.111 Mg_2Si + 0.033 Si		
					0.03810	0.10	0.10	0.111	0.096	0.141	0.090	0.055 Mg_2Si + 0.041 Si		
					0.04572	0.05	0.04	0.055	0.038	0.087	0.049	0.027 Mg_2Si + 0.011 Si		
					0.05334	0.03	0.02	0.033	0.019	0.053	0.026	0.016 Mg_2Si + 0.002 Si		
		48			0.03048	0.30	0.20	0.332	0.192	0.276	0.139	0.166 Mg_2Si + 0.025 Si		
					0.03810	0.20	0.15	0.221	0.144	0.204	0.081	0.111 Mg_2Si + 0.033 Si		
					0.04572	0.10	0.05	0.111	0.048	0.147	0.044	0.047 Mg_2Si + 0.015 Mg		
					0.05334	0.05	0.02	0.055	0.019	0.103	0.022	0.019 Mg_2Si + 0.017 Mg		

TABLE 5.—*Diffusion of Magnesium and Silicon in Aluminum from an Aluminum-alloy Core Containing an Excess of Magnesium Silicide and Silicon*

Specimen No.	Thermal Treatment		Solid Solubility in Al at 510° C.		Distance, x , Cm.	Concentration of Mg and Si in Al Coating						Molecular Per Cent Mg_2Si + Excess Atomic Per Cent Si	
	Temp., Deg. C.	Time, Hr.	Si, Atomic Per Cent	Mg_2Si , Molecular Per Cent		Observed				Calculated, Atomic Per Cent			
						Weight Per Cent		Atomic Per Cent					
						Mg	Si	Mg	Si				
													Mg
S10860	510	39	0.772	0.403	0.01778	0.15	0.20	0.166	0.192	0.186	0.233	0.083 Mg_2Si + 0.100 Si	
					0.02540	0.15	0.15	0.166	0.144	0.109			
					0.03302	0.03	0.04	0.033	0.038	0.038	0.043		0.016 Mg_2Si + 0.022 Si
					0.04064	0.01	0.02	0.011	0.019	0.010	0.015		
					0.04826	0.005	0.005	0.003	0.003				
					0.05588								
		73			0.02540	0.20	0.30	0.221	0.288	0.194	0.288	0.111 Mg_2Si + 0.177 Si	
					0.03302	0.10	0.20	0.111	0.192	0.116	0.190		0.055 Mg_2Si + 0.141 Si
					0.04826	0.02	0.10	0.022	0.096	0.031	0.068		
					0.05588	0.005	0.02	0.005	0.019	0.013	0.037		

^a This value was omitted in the determination of the average coefficient of diffusion.

referred to in the tables, the diffusion of magnesium and silicon into aluminum is fairly uniform. The abrupt drop in the magnesium concentration near the surface of the Alclad specimen S10862 (Table 2)

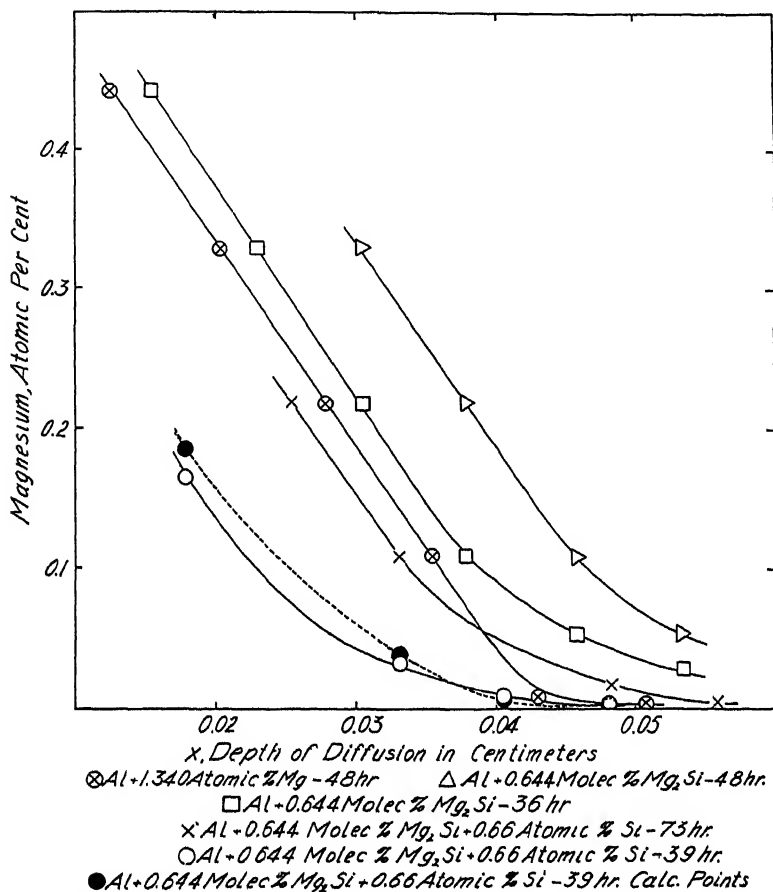


FIG. 6.—DEPTH-CONCENTRATION CURVES SHOWING DIFFUSION OF MAGNESIUM INTO ALUMINUM IN ALCLAD MATERIAL (Al2012A).

1. Unsaturated aluminum-magnesium alloy core heat-treated at 450° C.
2. Core containing excess magnesium silicide heat-treated at 510° C.
3. Core containing excess magnesium silicide and silicon heat-treated at 510° C.

was perhaps due to the volatilization of the magnesium because of prolonged heating.

The silicon concentration in the aluminum coating of the Alclad sample S10861 (Table 3), which had been heated for 57 hr. at 510° C., exceeded the solid solubility of silicon in aluminum. Microscopic examination of the cross section through the spectrographed area revealed particles of primary silicon. This indicated that the surface of the original miniature alloy ingot retained minute particles of silicon, which were

rolled into the soft aluminum coating. In view of this the quantitative data obtained were not used for the determination of the coefficient of diffusion.

The diffusion of magnesium and silicon into aluminum, as well as the effect of the presence of an excess of magnesium silicide and silicon on these rates of diffusion is shown in Figs. 6 and 7, which also include the curves, calculated by means of the coefficient of diffusion, for the progress

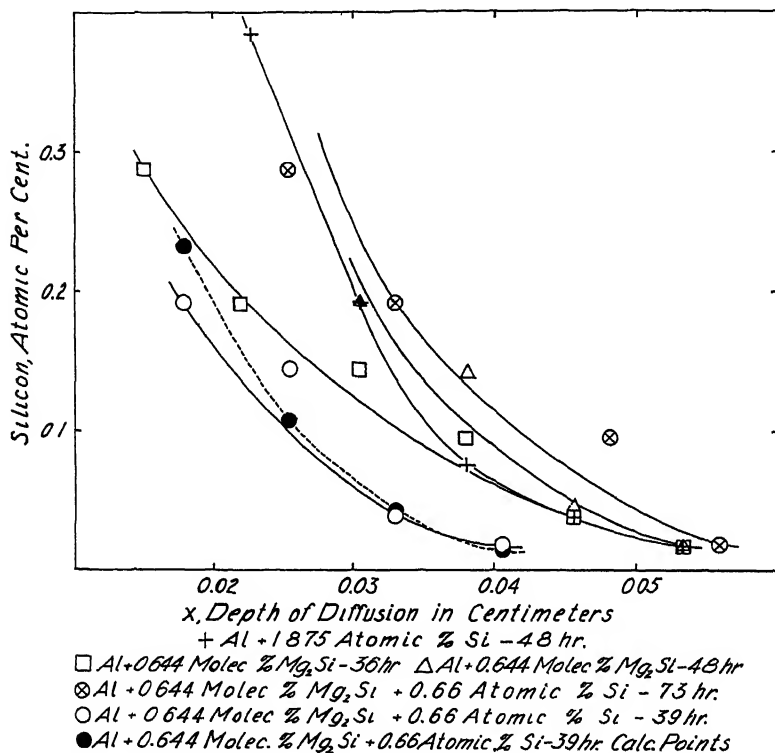


FIG. 7.—DEPTH-CONCENTRATION CURVES SHOWING DIFFUSION OF SILICON INTO ALUMINUM IN ALCLAD MATERIAL (Al2013A).

1. Core containing excess silicon heat-treated at 510° C.
2. Core containing excess magnesium silicide heat-treated at 510° C.
3. Core containing excess magnesium silicide and silicon heat-treated at 510° C.

of diffusion of magnesium and silicon from an alloy core containing excess magnesium silicide and silicon and corresponding to a thermal treatment of 39 hr. at 510° C.

INTERPRETATION OF EXPERIMENTAL RESULTS

The diffusion of magnesium and silicon into the high-purity aluminum coating is characterized by the formation of a solid solution without the formation of a new phase. Two cases must be considered; namely:

1. The diffusion of silicon and magnesium silicide from alloy cores containing an excess silicon and magnesium silicide.

2. The diffusion of magnesium from an aluminum-magnesium alloy core unsaturated with respect to magnesium.

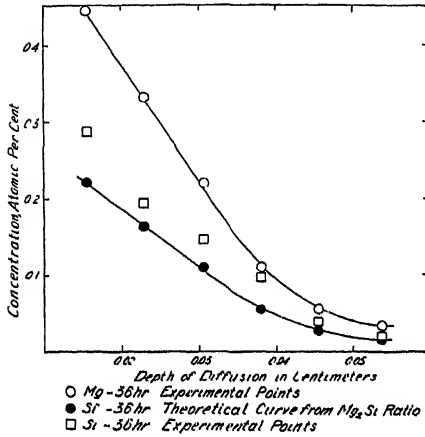


FIG. 8.

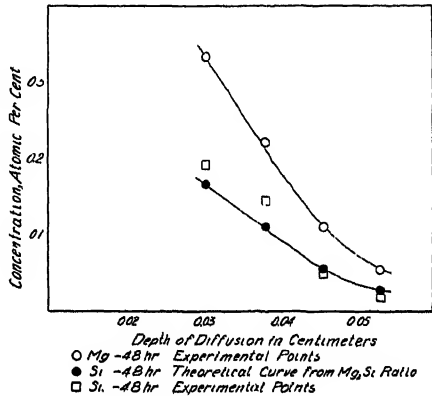


FIG. 9.

FIGS. 8 AND 9 —DEPTH-CONCENTRATION CURVES SHOWING THAT MAGNESIUM AND SILICON FROM AN ALLOY CORE CONTAINING EXCESS Mg_2Si TEND TO DIFFUSE IN THE APPROXIMATE RATIO OF THIS COMPOUND (A12014 AND A12015).

The relation of the concentration c of the diffusing metal to the time t and the depth of diffusion x is expressed by Fick's second law of diffusion:

$$\left(\frac{\delta c}{\delta t}\right)_x = D\left(\frac{\delta^2 c}{\delta x^2}\right)_t \quad [1]$$

The following limiting conditions must be considered for the solution of this partial differential equation:

1. Diffusion did not proceed to the surface of the metal coating.
2. When $t = 0$, $c = 0$ for all values of x greater than 0.
3. When $x = 0$, $c = c_0$ for all values of t (c_0 corresponds to the solid solubility of the diffusing metal in the alloy core).
4. When $t = 0$, $c = c_0$ for all values of x less than 0.

The first three conditions apply to case 1, the diffusion of silicon and magnesium silicide into aluminum from an alloy core saturated with respect to the diffusing materials. By assuming that the alloy core remains saturated at the interface, the integration of equation 1 yields the following relationship:

$$c = \frac{2c_0}{\sqrt{\pi}} \frac{x}{2\sqrt{Dt}} \int_0^\infty e^{-y^2} dy \quad [2]$$

where c_0 = the solid solubility of the diffusing metal in the aluminum-alloy core at the temperature of heat-treatment.

c = its concentration in the aluminum coating corresponding to a time t of thermal treatment and a depth of penetration x .

D = the coefficient of diffusion.

y = an integration variable the magnitude of which is dependent upon the observational errors.

Since

$$\frac{\sqrt{\pi}}{2} = \int_0^{\infty} e^{-y^2} dy$$

it follows that

$$\int_{\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-y^2} dy = \frac{\sqrt{\pi}}{2} - \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy \quad [3]$$

Substituting this value in equation 2 and simplifying the expression:

$$\frac{c_0 - c}{c_0} = \frac{2}{\sqrt{\pi_0}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy \quad [4]$$

The values $\frac{x}{2\sqrt{Dt}}$ corresponding to all values of the integral are given in the Smithsonian Physical Tables⁶. Equation 4 describes the progressive change in concentration of the diffusing silicon in the aluminum coating. Thus, for example, at 510° C. c_0 , the solid solubility of silicon in the aluminum-silicon alloy core corresponds to 0.772 atomic per cent. After 48 hr. of heat-treatment at 510° C. the amount of silicon c that had penetrated a depth x of 0.03048 cm. (0.012 in.) in the high-purity aluminum coating corresponded to 0.192 atomic per cent. Therefore,

$$0.7512 = \frac{2}{\sqrt{\pi_0}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy$$

The upper limit of the integral in this equation corresponds to 0.815 according to the tables. Therefore:

$$\frac{x}{2\sqrt{Dt}} = 0.815$$

and

$$D = \frac{x^2}{4t (0.815)^2}$$

sium may have diffused to the surface of the coating, which, of course, would render doubtful the value for the coefficient of diffusion of magnesium. The diffusion of silicon in the aluminum coating did not appear to have progressed to the surface. However, the experimental data appear to indicate that the diffusion of magnesium from the binary aluminum-magnesium alloy and the diffusion of silicon from the binary aluminum-silicon alloy into their respective high-purity aluminum coatings are of the same order of magnitude.

It is of interest that the simultaneous presence of definite amounts of magnesium and silicon in the alloy core affects the rates of diffusion of these elements. Thus, the results of the analytical data for the Alclad sample (S11302), which contained excess magnesium silicide in the alloy core, showed that the simultaneous presence of magnesium and silicon in the ratio of Mg_2Si decreased the amount of diffused silicon. The experimental results summarized in Table 4 and illustrated by Figs. 8 and 9 suggest that the magnesium and silicon tend to diffuse into the aluminum coating in the approximate ratio of Mg_2Si if the alloy core is an aluminum-magnesium silicide alloy. However, if the alloy core contains excess silicon and magnesium silicide (Alclad sample S10860) the diffusion of magnesium in aluminum is greatly diminished, with the result that the Alclad coating contains an excess silicon (Table 5). This excess silicon necessarily will have an effect on the corrosion resistance of the Alclad material.

ACKNOWLEDGMENTS

The author wishes to express her indebtedness to Mr. A. W. Petrey, under whose supervision the spectrographic analyses were carried out, and to Mr. K. von den Steinen and Mr. V. Thornburg for their helpful suggestions.

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Coefficient of Equivalence of Iron with Respect to Aluminum in Aluminum Bronze

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JUNIOR MEMBER

(New York Meeting, February, 1936)

It is well known that iron markedly improves the physical properties and casting characteristics of aluminum bronzes. The use of 1 to 4 per cent iron as the principal modifying addition has become common practice in many foundries melting aluminum bronzes. Although the beneficial effects of iron are unquestioned, there is some uncertainty regarding the structural changes caused by it in the basic copper-aluminum system. It is agreed that a new constituent appears in abundance when the iron content reaches 2 to 4 per cent. This constituent, which frequently occurs in shapes resembling clover leaves, is sometimes assumed to be an aluminum-iron intermetallic compound. If this were correct we might expect a change in the structural relationships of the matrix in the direction of decreased aluminum content. On the other hand, it has been reported that iron has a negligible effect in altering the fundamental relationships of copper-aluminum alloys¹.§ Others^{2,3} have reported an additive coefficient.

Apparently it will be necessary to know the equilibrium relationships between the phases of the copper-aluminum-iron alloy system to establish any such theory as fact. When this has been done it may very well be that a further revision in the structural relationships may be necessary to describe the changes to be expected in commercial cast alloys. It was with this latter problem before them that the authors attempted to determine the change in the copper-aluminum relations with respect to iron.

OBJECTS OF THE INVESTIGATION

In certain investigations carried out by the authors for a plant producing a large tonnage of cast aluminum bronzes the structures

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§ References are at the end of the paper.

obtained varied with the method of introduction of iron. This investigation was carried out with the following ends in view:

1. To determine whether the method of introduction of the iron has any effect on the structure obtained.
2. To determine the effect of iron on the constituents and ascertain whether a coefficient of equivalence does exist.
3. To determine the departure from equilibrium under routine casting of small shapes.
4. To carry out certain preliminary work with a view to attacking, later, the copper-iron-aluminum equilibrium diagram.

PREPARATION AND ANALYSIS

In order to cover the commercial field, as well as to introduce the variable of the manner of introduction of the iron, three series of alloys were made. The *X* and *Y* series were prepared by first alloying commercial copper and aluminum in the desired proportions and then adding Armco ingot iron in the desired amounts. The relationship between the copper and aluminum was maintained fairly constant while the percentage of iron varied.

In the *Z* series an alloy was first made up from iron and aluminum in the ratio of approximately 3 to 1, and to this molten copper was added to obtain the desired compositions. The relationship between the iron and aluminum was fairly constant while the copper varied. To insure homogeneity each heat was melted, pigged, then remelted and cast into test bars 14 by 1 by 1 in. The molds were inclined and large risers and sprues were used, because of the shrinkage characteristics of these alloys.

The *W* series was made from high-conductivity, oxygen-free copper and high-purity aluminum. The specimens were prepared by making up an alloy corresponding approximately to CuAl_2 and working this down to the desired composition by melting, adding a part of the copper, pigging, remelting and adding the remainder of the copper to adjust the composition. They were found to be free from iron.

Great care was exercised in the analysis, and all analyses were run in triplicate. Copper was determined electrolytically; iron and aluminum were precipitated as the hydroxides and ignited. Iron was reduced in a Jones Reductor and titrated with potassium permanganate. The series of alloys are indicated on the ternary composition diagram in Fig. 1 and the individual analyses in Table 1.

HEAT-TREATMENT AND EXAMINATION

Sections of the test bars about $\frac{5}{8}$ in. long were used for heat-treatment to determine the phase boundaries. In each specimen a hole was drilled

for the insertion of a thermocouple. Each specimen was suspended in a vertical tube electric furnace; heated to 100° C. above the suspected transformation temperature; cooled to this temperature; held there for

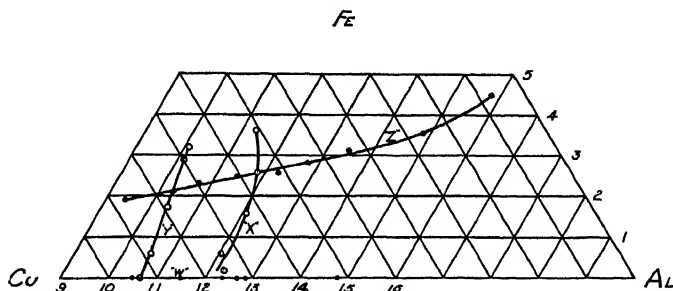


FIG. 1.—COMPOSITIONS OF ALLOYS.

2 hr. and then quenched by dropping into a container filled with ice-brine. Every precaution was observed to insure accurate and dependable results. The surface used for microscopic examination was a cross

TABLE 1.—*Chemical Analyses*

Alloy No.	Composition, Per Cent			Alloy No.	Composition, Per Cent		
	Copper	Aluminum	Iron		Copper	Aluminum	Iron
X0	87.52	12.40	0.16	Z3	83.30	13.48	3.14
X1	87.34	12.04	0.56	Z4	84.40	12.76	2.81
X2	86.14	12.10	1.57	Z5	85.12	12.26	2.58
X3	85.64	11.86	2.58	Z6	86.03	11.45	2.49
X4	85.00	11.31	3.60	Z7	86.88	10.74	2.35
				Z8	87.76	10.30	2.08
Y0	89.30	10.65	0.00	Z9	88.63	9.39	1.93
Y1	88.78	10.55	0.60				
Y2	87.86	10.36	1.73	W1	10.52	89.48	0.00
Y3	87.05	10.14	2.89	W2	11.52	88.48	0.00
Y4	86.85	10.10	3.17	W3	12.37	87.64	0.00
				W4	12.66	87.38	0.00
Z1	79.62	15.82	4.46	W5	12.89	87.14	0.00
Z2	81.88	14.84	3.53	W6	14.82	85.20	0.00

section of the original bar and the first surface to strike the quenching bath. No unusual difficulties were encountered in polishing and etching.

DETERMINATION OF EUTECTOID TEMPERATURE

The phase boundaries were determined by a heat-treatment and quenching procedure rather than by thermal analysis. It appears to be a reasonably accurate method, since the phases encountered in these

alloys are readily retained at room temperature by quenching. The beta phase, to be sure, has been proved to be partially transformed to some intermediate form, which has been called beta prime⁴. However, it retains a characteristic acicular appearance, which is easily distinguished from alpha or delta.

The eutectoid transformation, $\beta \rightarrow \alpha + \delta$, of the copper-aluminum alloys is known to be very slow and the problem becomes one of establishing equilibrium before quenching from temperatures below 570° C. In this respect the authors found that the iron-bearing alloys transform much more rapidly than the iron-free. It is likely that the rate of this transformation is responsible for the wide range of eutectoid temperatures, 515° to 570° C., reported in the early literature. Interestingly enough, Curry in 1907 reported 570° C. and 12.5 per cent aluminum at the eutectoid. This temperature, 570° C., checks remarkably the careful work of Smith and Lindlief, recently reported to this society. Smith and Lindlief, in their study of the decomposition of the beta phase of a copper-aluminum alloy of 11.87 per cent aluminum⁴, determined that the transformation of the beta phase in forming the eutectoid did not commence for 1 hr. and was not completed until after 10 hr. at a temperature of 565° C.

With the object of determining the speed of the eutectoid transformation in iron-bearing alloys of copper and aluminum, specimens were cooled to 560° C., held for 2 hr., and quenched. The transformation at this temperature was completed in 2 hr. In like manner, specimens heated to 570° C., held 2 hr. and quenched, exhibited complete transformation. Figs. 2 and 3 are photomicrographs of specimens quenched at 560° and 570° C., showing the transformation of alpha plus eutectoid plus compound to alpha plus beta plus compound. The speed of the eutectoid transformation in the iron-bearing copper-aluminum alloys observed in these determinations is more rapid than that noted by Smith and Lindlief.

The results of these tests indicate a eutectoid transformation temperature of 568° C. for all alloys studied. Iron has very little influence on this temperature. In order to determine this, a number of alloys, representing all the types studied, were heated to 570° C., held for 6 hr., then quenched. All eutectoidal structure was transformed to beta. A parallel set of specimens was heated to 566° C., held for 6 hr., then quenched. No transformation to beta was observed. Similar experiments on cooling and other results based on 24-hr. treatments at 568° C. indicated a eutectoid transformation at $568 \pm 2^\circ$ C. for all the alloys considered.

COPPER-ALUMINUM ALLOYS

The results of the tests made on the X, Y and Z series indicated to us that our fundamental copper-aluminum relations were being displaced,

with respect to the Stockdale^{5,6} equilibrium diagram, by some factor other than iron. The phase boundaries of these alloys were determined by the quenching method already described. The quenching tempera-

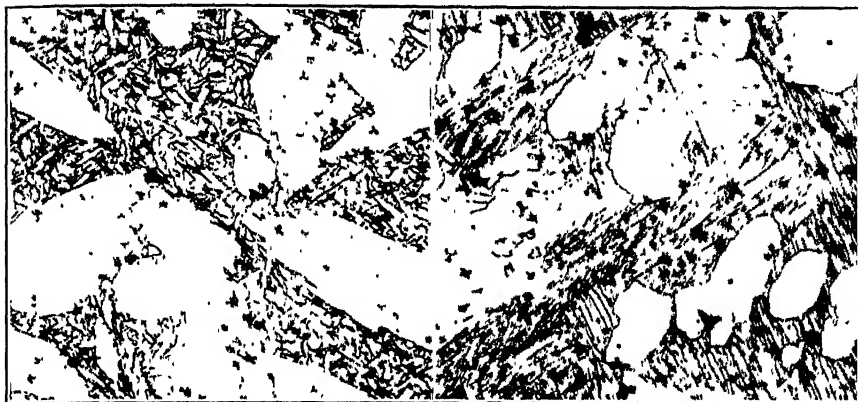


FIG. 2.

FIG. 3.

FIGS. 2 AND 3.—Zr. $\times 500$. ETCHANT, AMMONIUM PERSULFATE.

2. Quenched at 560° C. Alpha plus eutectoid plus compound.

3. Quenched at 570° C. Alpha plus beta plus compound.

tures were at 10° C. intervals, consequently the transformation temperatures are within 5° C. The phases present were readily established

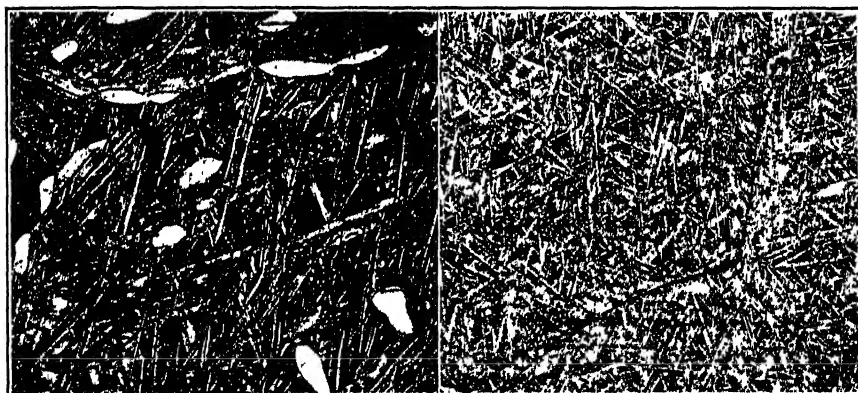


FIG. 4.

FIG. 5.

FIGS. 4 AND 5.—Y0. $\times 100$. ETCHANT, $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

4. Quenched at 840° C. Alpha plus beta.

5. Quenched at 850° C. Beta.

by microscopic examination. For example, Figs. 4 and 5 show the disappearance of the alpha phase upon quenching at 850° C. Alpha is seen to be present in an alloy quenched at 840° C. Figs. 6 and 7 show a similar transformation between 640° and 650° C. from alpha plus beta plus compound to beta plus compound. Figs. 8 and 9 show the trans-

formation between 560° and 570° C. from eutectoid plus compound to beta plus compound.

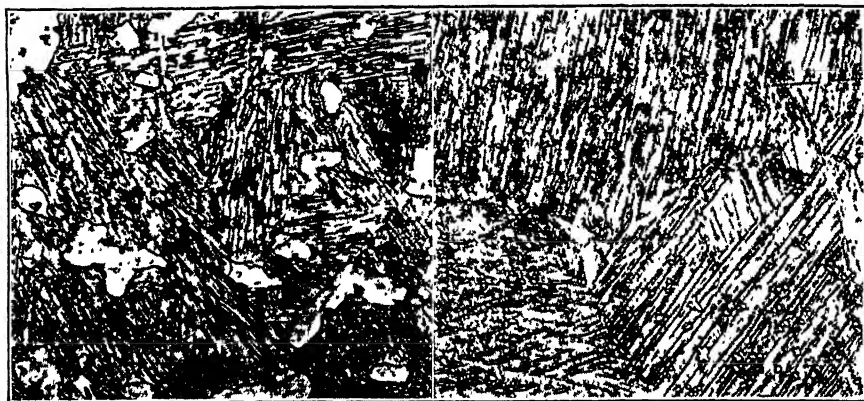


FIG. 6.

FIG. 7.

FIGS. 6 AND 7.—Z5. $\times 500$. ETCHANT, AMMONIUM PERSULFATE.

6. Quenched at 640° C. Alpha plus beta plus compound.

7. Quenched at 650° C. Beta plus compound.

The *W* series was then prepared from pure materials to determine the transformation range of iron-free cast alloys. In Fig. 10 Stockdale's diagram has been modified by raising the eutectoid temperature

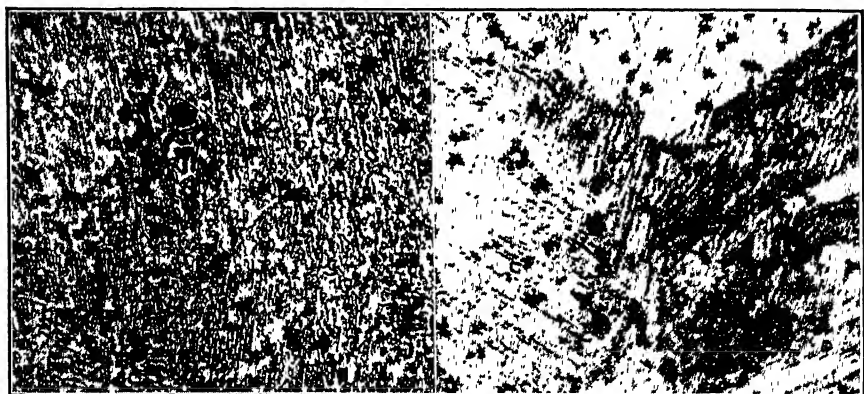


FIG. 8.

FIG. 9.

FIGS. 8 AND 9.—Z4. $\times 500$. ETCHANT, FERRIC CHLORIDE.

8. Quenched at 560° C. Eutectoid plus compound.

9. Quenched at 570° C. Beta plus compound.

to 568° C. The dotted diagram represents the phase boundaries drawn to correspond to the transformations of the *W* alloys. The data for these transformations are summarized in Table 2. The displacements are quite constant, the average being 0.51 per cent aluminum, in the direction of increased aluminum content.

The dotted lines in Fig. 10 bear a close resemblance to Curry's 1907 diagram. The authors are unable to explain the general shift of about

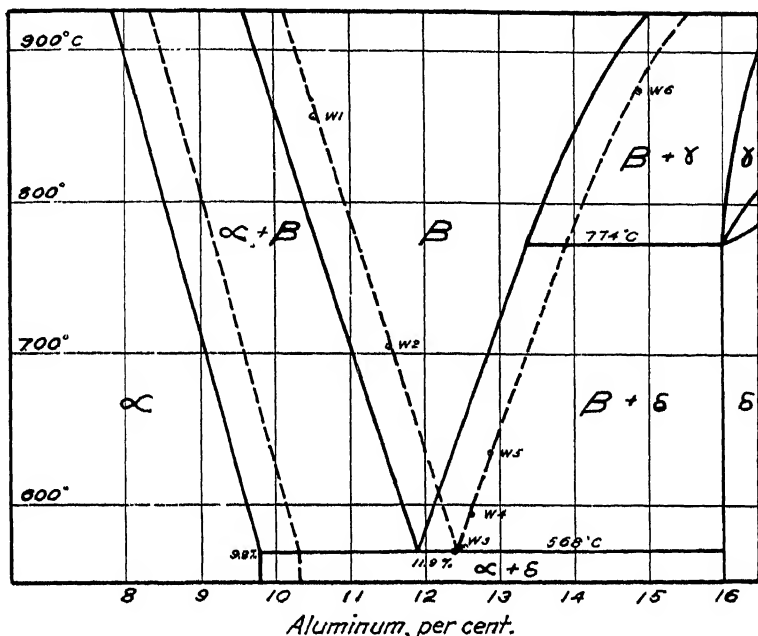


FIG. 10.—TRANSFORMATION TEMPERATURES OF W SERIES (IRON-FREE) COMPARED TO COPPER-ALUMINUM EQUILIBRIUM DIAGRAM.

TABLE 2. Transformation Temperatures and Composition Displacements

Alloy No.	Trans. Temp., Deg. C.	Aluminum, Per Cent		Displacement, Per Cent Al
		1 ^a	2 ^b	
W1	855	10.52	10.02	0.50
W2	705	11.52	11.00	0.52
W3	570	12.37	11.90	0.47
W4	595	12.66	12.10	0.56
W5	635	12.89	12.37	0.52
W6	875	14.82	14.35	0.47
				Average 0.51

^a Actual percentage of aluminum by analysis.

^b Percentage of aluminum on modified Stockdale diagram for alloy transforming at same temperature.

0.5 per cent aluminum compared with the commonly accepted diagram. While the alpha and near-alpha alloys of this system freeze over a range of temperatures and are subject to dendritic segregation, the eutectoidal

alloys freeze at nearly a constant temperature, and should be more nearly homogeneous as cast.

EFFECT OF IRON ON COPPER-ALUMINUM ALLOYS

The transformation temperatures of the *X* and *Y* series are referred to the *W* series diagram in Fig. 11; likewise the transformations of the *Z* series are referred to the *W* series in Fig. 12. Table 3 gives the transformation temperatures and composition displacement data of *X*, *Y* and

TABLE 3.—Transformation Temperatures and Composition Displacement

Alloy No.	Trans. Temp., Deg. C.	Aluminum, Per Cent			Displace- ment, Per Cent Al	Iron, Per Cent	Per Cent Al Displacement (Col. F)
							Per Cent Fe (Col. G)
A	B	C ^a	D ^b	E ^c	F	G	H
X0	565	12 40	12.42	12 41	0.01	0.16	0 06
X1	615	12 04	12 12	12 09	0.03	0 56	0.05
X2	585	12 10	12 30	12 27	0.03	1.57	0 02
X3	635	11 86	12.18	11 95	0.23	2.58	0 09
X4	675	11 31	11 75	11 71	0.04	3.60	0.01
Y0	845	10.65	10 65	10 59	0.06	0.00	
Y1	845	10.55	10 62	10.59	0.03	0.60	0 05
Y2	875	10 36	10.54	10.39	0.15	1 73	0.09
Y3	895	10 14	10.44	10.27	0.17	2.89	0.06
Y4	895	10 10	10 42	10 27	0 15	3.17	0 05
							Average 0.05
Z1	895	15 82	16.57	15 01	1.56	4 46	0.349
Z2	815	14.84	15 40	14.23	1.17	3.53	0.332
Z3	645	13 48	13 92	12 99	0.93	3.14	0.296
Z4	565	12 76	13.11	12 41	0.70	2.81	0.249
Z5	645	12 26	12 60	11 89	0.71	2 58	0.275
Z6	795	11.45	11.73	10.91	0.82	2 49	0.329
Z7	895	10 74	11 00	10.27	0.73	2.35	0.310
Z8	625	10.30	10.52	10.01	0.51	2 08	0.245
Z9	785	9 39	9.57	9.13	0.44	1.93	0.228
							Average 0.31

^a Actual percentage of aluminum by analysis.

^b Percentage of aluminum by analysis on iron-free basis.

^c Percentage of aluminum as determined by *W* series diagram for alloy transforming at same temperature.

Z alloys. The transformation temperatures were determined as before. The displacement of the *X* and *Y* alloys from the previously determined cast structure is small, the displacement coefficient averaging only 0.05 per cent aluminum for each per cent of iron, so that apparently iron has very little tendency to alter equilibrium relationships in alloys

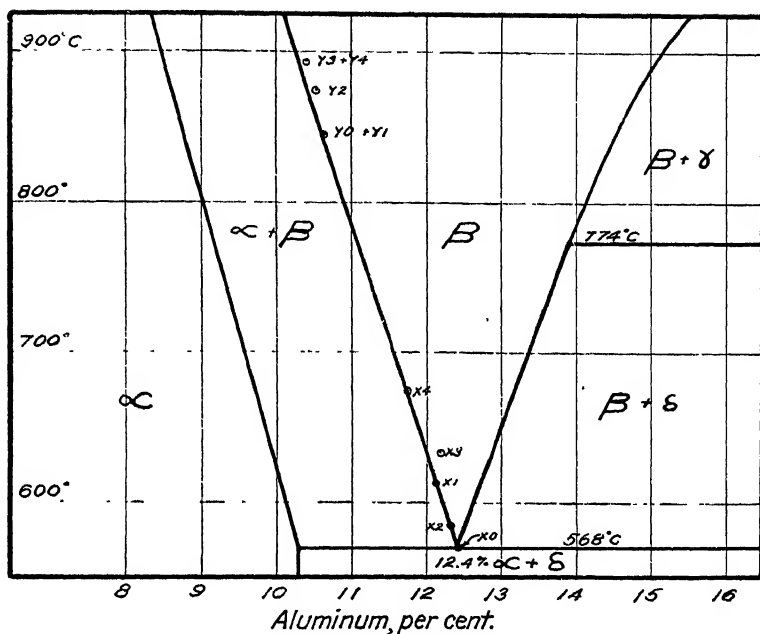


FIG. 11.—TRANSFORMATION TEMPERATURES OF X AND Y ALLOYS AS COMPARED TO W ALLOYS.

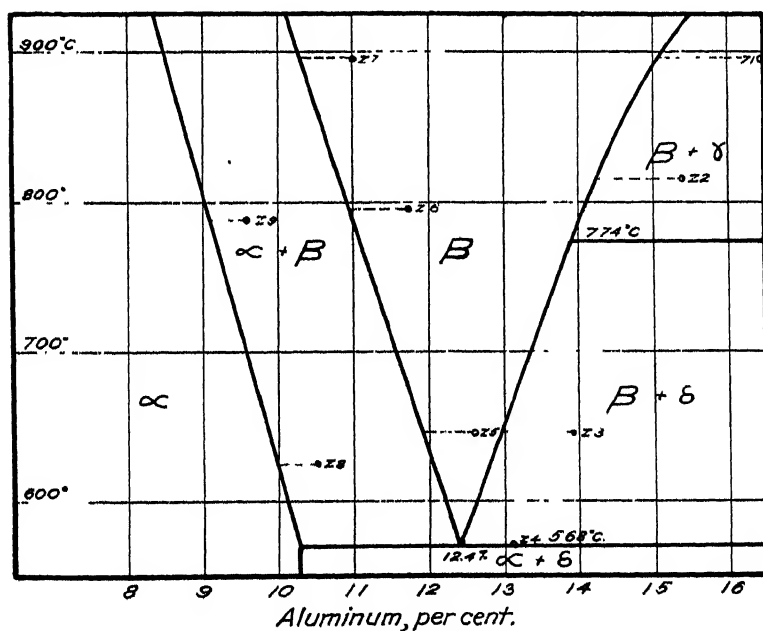


FIG. 12.—TRANSFORMATION TEMPERATURES OF Z ALLOYS AS COMPARED TO W ALLOYS.

of this type (column H, Table 3). The average displacement caused by each per cent of iron in the Z series is 0.31 per cent aluminum (column H, Table 3).

Since the only variable introduced was the method of melting the alloys, this seemingly impossible result must be ascribed, for the present at least, to the melting practice.

CONCLUSIONS

1. Iron in amounts up to 4 per cent, introduced as such, does not alter the copper-aluminum solid-solution relationships of cast alloys.

2. Iron in amounts up to 4 per cent, introduced as an iron-aluminum intermetallic compound, does alter the copper-aluminum solid-solution relationships of cast alloys.

3. The presence of iron up to 4 per cent hastens materially the speed of the eutectoid transformation on cooling.

4. Iron up to 4 per cent has very little effect on the temperature of the eutectoid transformation.

ACKNOWLEDGMENTS

The writers wish to acknowledge the cooperation of Ampco Metals, Inc., in preparing certain of the alloys.

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DISCUSSION

(Gilbert E. Doan presiding)

G. E. DOAN,* Bethlehem, Pa.—It adds interest to the study of physical metallurgy to find some more attention being given to the matter of the rate at which equilibrium is approached, rather than only to the static conditions of structure that obtain when that equilibrium is reached. We have been taught, of course, that equilibrium does not change with the direction from which it is approached, but in industrial operation probably we do not deal very frequently with equilibrium, so that this paper seems to lend itself to discussion from a number of different viewpoints.

E. H. DIX, JR.,† New Kensington, Pa.—I did not have an opportunity to read the paper before coming to the meeting, so that I am just a little bit confused in relation to the comparison with the work of this paper and the Stockdale equilibrium diagram. I am not sure, for instance, whether this difference in the phase boundaries

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† Metallurgist, Aluminum Research Laboratories.

is a result of casting conditions in which equilibrium has not been obtained or whether annealing has been carried out for sufficient length of time to produce equilibrium, and the authors think even under those conditions the casting has had an effect. It might be interesting to all of us to have that point clarified.

J. L. BRAY.—No, this is not an equilibrium diagram. In making these articles of aluminum bronze, we were concerned only with the results obtained on casting. This is not an equilibrium diagram for the articles were not annealed. We did get certain proportions of alpha and beta and these did not correspond to the proportions called for by the Stockdale diagrams.

We were interested from our own standpoint in these cast alloys. In connection with the chairman's remarks, I believe there is something to this method of alloying. At the present time, in a cooperative arrangement with one of the steel companies, we are working on a low-alloy copper-nickel-chromium steel. If the copper nickel and chromium are added as solid alloys to the open-hearth furnace one set of properties is obtained; if the copper nickel and chromium are melted and made into an alloy in a small gas-fired furnace and then added to the open-hearth furnace, we get another set. This steel company is not spending thousands of dollars, as it is, just for amusement, and it is not conjecture, for hundreds of tons have been made. It does seem ridiculous, and I admit it, but such are the facts. The alloys of aluminum and copper produced under otherwise identical conditions do vary as indicated.

C. G. FINK,* New York, N. Y.—Was there any difference in the general characteristics of the metal due to difference in oxygen content?

J. L. BRAY.—We did not determine that.

C. G. FINK.—It would be very difficult.

J. L. BRAY.—Yes, and we were not warranted in doing it.

C. G. FINK.—But why start out with oxygen-free copper and remelt?

J. L. BRAY.—We had to correlate this from plant conditions and it had to be done in the plant.

MEMBER.—Which alloy of iron was added?

J. L. BRAY.—It was added as an aluminum alloy.

S. ROLLE,† New York, N. Y.—I think Professor Fink has put his finger on the reasons for the discrepancies, considering our limited experience. Taking for example, the analysis of alloy Z-1, the total comes to 99.9 per cent—leaving one-tenth of one per cent to be accounted for. I wonder whether Professor Bray has attempted to determine the oxygen content and other elements so as to bring the total up to 100 per cent.

J. L. BRAY.—No, the W series was made up so far as oxygen contamination would go, in exactly the same way as the Z series.

G. E. DOAN.—There seem to be a great many variables involved. These variables may have been held constant when the iron was added as ingot iron as well as when it was added as compound. Yet, the results are quite different.

* Head, Division of Electrochemistry, Columbia University.

† U. S. Metals Refining Co.

T. A. WRIGHT,* New York, N. Y.—I am going to introduce another variable. Page 342 gives displacement of aluminum as roughly 0.5 per cent, but a note of caution should be entered as to metallurgists accepting the analyses (and formulating basic theories or conclusions) on results supplied by the chemists, without considering the precision. Sampling of such material is not necessarily an easy question to solve. The actual determination by chemical analysis by a direct method on aluminum itself is not such an easy thing as one might expect. One should consider the precision the chemist has been able to meet under the conditions governing. The precision might be no greater than 0.25 per cent and apparently often in routine aluminum determinations, for the amounts of aluminum present in this case, it may not reach that.

It is quite different from the determination of copper in similar amounts in which one might attain results within 0.05 per cent or at least 0.10 per cent, although in many small plants making routine copper determinations 0.25 per cent would be considered sufficient.

While it is often customary to take results for some one element by difference, there are other occasions where it is not justified and the point certainly should be kept in consideration.

* Secretary and Technical Director, Lucius Pitkin, Inc.

Physical Properties of Soft Solders and the Strength of Soldered Joints

By B. W. GONSER,* MEMBER A.I.M.E., AND C. M. HEATH*

(New York Meeting, February, 1936)

SOFT solders are used principally in the automotive, can-making, building construction and electrical industries, but their field of usefulness extends well beyond these principal users to a vast list of miscellaneous applications where metal joints are required. The most common soft solders and the only ones considered in this discussion are those composed of lead and tin, with or without various relatively small percentages of impurities or additions. A small amount of antimony is often purposely added. As an indication of the importance of these lead-tin solders, 8620 long tons of tin were consumed in 1934 in the United States for making new solder, and during most of 1935 from 900 to 1000 long tons often were used each month. In addition, many thousands of tons of secondary solder are recirculated annually.

A great many factors influence the properties of joints made with soft solders. Fluxes and the fluxing procedure used to prepare the surfaces to be joined in order to give a true metal-to-metal contact are among the most important of these factors. The temperatures used, cleanliness of the work and general soldering technique have their effect, but when results are unsatisfactory they are usually attributed to the metallic solder itself and the raw materials from which it is made. Sometimes criticism of the solder is justified. The wrong composition may be chosen for a given job, impurities may be present that ruin certain desired qualities, or uniformity may be lacking. A solder may even be looked upon with suspicion because of its ancestry, regardless of its true composition and behavior. To clarify the effect of slight differences in composition as found in commercially refined solders, a comparison of properties of solders grouped according to their origin has been undertaken.

This investigation seeks to give practical information on the properties of tin-lead solders produced from virgin metals, from commercially refined secondary solder, and from an electrolytically refined crude

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* Metallurgist and Assistant Metallurgist, respectively, Battelle Memorial Institute, Columbus, Ohio.

lead-tin refinery product. This paper gives the results of physical tests on the various solders as massive metal, and of tests on the comparative strengths of brass lap joints made with them. Because of the very great importance of small changes in operating technique when working with solders, it is considered necessary to give essential details of experimental procedure.

SOLDER COMPOSITIONS

Four series of solders were used in this work:

Series A. Virgin metals, Straits tin and desilverized lead.

Series B. Secondary solder, adjusted with Straits tin and desilverized lead.

Series C. Electrorefined crude solder, adjusted with Straits tin.

Series D. Electrorefined crude solder, adjusted with Chinese tin.

In each series, eight metal compositions were used to cover the range of the most commonly employed solders. These were 15, 20, 25, 30, 35, 40, 50 and 63 per cent tin, respectively, the remainder being lead plus 0.12 per cent antimony, and impurities. (No 15 per cent tin composition was made for series D alloy.)

Antimony was purposely added to each alloy to give a uniform amount (0.12 per cent Sb) within the usual specifications^{1*}. The source and production of the electrolytic solder used has been described by Hermsdorf and Heberlein². Since it contained only 20 to 25 per cent tin, considerable tin was added in the high-tin compositions. Secondary solder came largely from scrapped automobile radiators.

In order to determine the impurities present, spectroscopic analyses were necessary because of the low percentages involved. Results are given in Table 1.

The chief differences between the composition of virgin metal solder and the other solders tested were the relatively high silver content of the secondary solder, the somewhat greater purity of electrolytic solder, and the contamination of series D electrolytic solder by the addition of Chinese tin.

Although precautions were taken to prevent contamination of the samples with dust, it is doubtful whether calcium, magnesium and silicon were actually present in the metal in the amounts indicated. These are considered to be relatively unimportant impurities.

PHYSICAL TESTS

Solder is normally used as a joining material between other metal pieces and its behavior in this respect is of most practical importance, but physical tests on the solder alone have some fundamental value in determining the effect of small differences in impurity content. These

* References are at the end of the paper.

small influences due to differences in composition might be completely overshadowed in joint tests where many factors, such as the flux used, surface condition of the base metal, contamination by the base metal,

TABLE 1.—*Results of Spectrographic Analyses*

Sample ^a		Cu, Per Cent	Ag, Oz. per Ton	Bi, Per Cent	Fe, Per Cent	Ni, Per Cent	Insol., Per Cent	Mg, Per Cent	Si, Per Cent
Series	Per Cent Sn								
A	15	0.003	0.25	0.015	0.001	0.0005	0.0002	0.0005	0.0001
	20	0.003	0.25	0.015	0.001	0.0005	0.0002	0.001	0.0001
	25	0.002	0.25	0.012	0.001	0.0005	0.0005	0.0005	0.0001
	30	0.002	0.25	0.012	0.001	0.0005	0.0005	0.0001	0.0001
	35	0.002	0.25	0.010	0.001	0.0005	0.0005	0.0002	0.0001
	40	0.002	0.25	0.010	0.001	0.0005	0.001	0.0002	0.0001
	50	0.002	0.25	0.010	0.002	0.0002	0.001	0.0001	0.0001
	63	0.002	0.25	0.010	0.002	0.0005	0.002	0.0001	0.0001
B	15	0.003	2.0	0.015	0.0005	0.0001	0.0002	0.0002	0.0001
	20	0.002	2.0	0.015	0.0005	0.0001	0.0002	0.0002	0.0001
	25	0.002	2.0	0.015	0.0005	0.0002	0.0005	0.001	0.0001
	30	0.002	2.0	0.015	0.001	0.0002	0.0005	0.0005	0.0002
	35	0.003	2.0	0.015	0.001	0.0005	0.0005	0.0002	0.0002
	40	0.002	2.0	0.015	0.001	0.0005	0.0005	0.0002	0.0001
	50	0.002	2.0	0.015	0.002	0.0008	0.001	0.0002	0.0001
	63	0.002	2.0	0.015	0.002	0.001	0.001	0.0002	0.0001
C	15	0.003	0.25	0.010	0.001	0.0001	0.0002	0.0002	0.0005
	20	0.001	0.25	0.010	0.001	0.0001	0.0002	0.0005	0.0005
	25	0.001	0.15	0.008	0.001	0.0002	0.0005	0.001	0.0002
	30	0.001	0.15	0.008	0.002	0.0002	0.0005	0.0005	0.0005
	35	0.002	0.10	0.005	0.002	0.0005	0.0005	0.002	0.0005
	40	0.002	0.10	0.005	0.002	0.0005	0.001	0.0002	0.0002
	50	0.002	0.05	0.002	0.003	0.0005	0.001	0.0005	0.0001
	63	0.002	0.05	0.002	0.003	0.001	0.001	0.0005	0.0001
D	20	0.005	0.05	0.001	0.001	0.0005	0.0005	0.0001	0.0001
	25	0.005	0.05	0.001	0.002	0.0005	0.0005	0.0005	0.0001
	30	0.008	0.10	0.003	0.002	0.0005	0.001	0.0002	0.0001
	35	0.008	0.10	0.003	0.005	0.001	0.001	0.0002	0.0001
	40	0.010	0.15	0.005	0.005	0.001	0.001	0.0001	0.0001
	50	0.020	0.20	0.005	0.008	0.001	0.002	0.0002	0.0001
	63	0.010	0.25	0.008	0.010	0.001	0.002	0.0005	0.0001

^a Calcium was present to the extent of 0.0001 per cent in all samples. The following were not detected in any of the samples: Zn, Al, P, As, Au, Ba, Cd, Co, Cr, Ga, Ge, Hg, Ii, Mn, Mo, Na.

soldering technique, etc., would interfere. Physical tests made on the solders under consideration covered electrical conductivity, Charpy impact, tensile strength and shear strength.

Casting.—After trying various methods of melting solder, a No. 4, bottom-pouring Rowell cast-iron ladle was adopted. This was heated by a gas flame protected by a burner guard. In this way flexibility and rapid heating were obtained without sacrificing satisfactory temperature control. A thermocouple protected by a graphite tube served to stir the melt as well as to indicate the temperature.

Melts were made from two pound pigs of solder, using only enough to make the required number of specimens from each alloy. Remelts of test

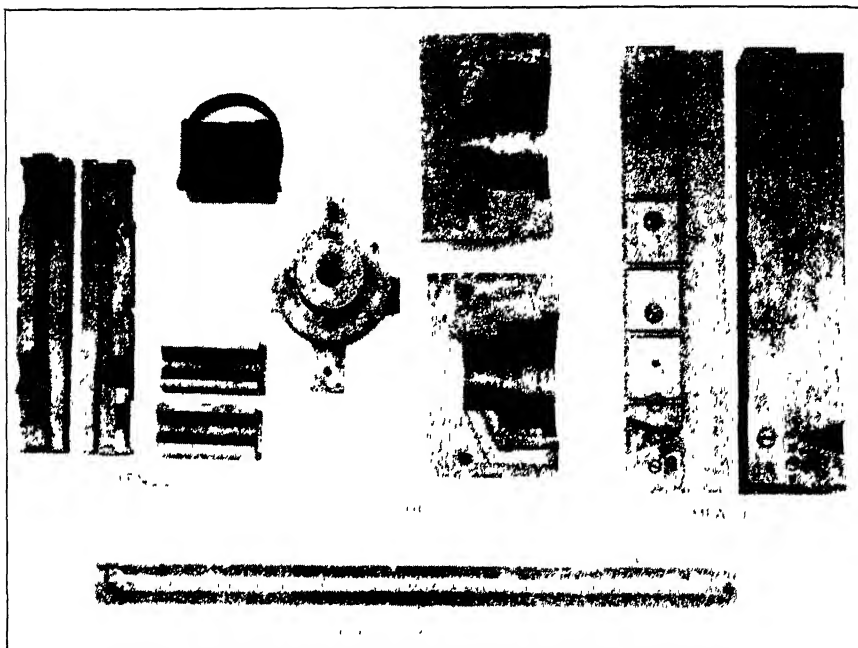


FIG. 1.—MOLDS FOR PHYSICAL TEST SPECIMENS OF SOLDER.

specimens with their respective gates were at times made in checking results, but fresh solder was always used in making final tests. Powdered rosin was used as the flux.

The steel molds used for casting test specimens are shown in Fig. 1. These were smoked with acetylene soot to give a very light coating before making each casting. This operation required considerable skill, as too heavy a coating gave excessive shrinkage; too little soot gave poor castability. The tensile specimen was the most sensitive in this respect, but with care specimens free from troublesome dimensional shrinkage were obtainable.

In pouring, it was necessary to keep the ladle as close to the sprue as possible, to eliminate drossing action caused by excessive turbulence. Specimens were air-cooled upon removal from the mold. By timing all

operations, after preliminary tests indicated the best operating technique, very close duplication of conditions was secured.

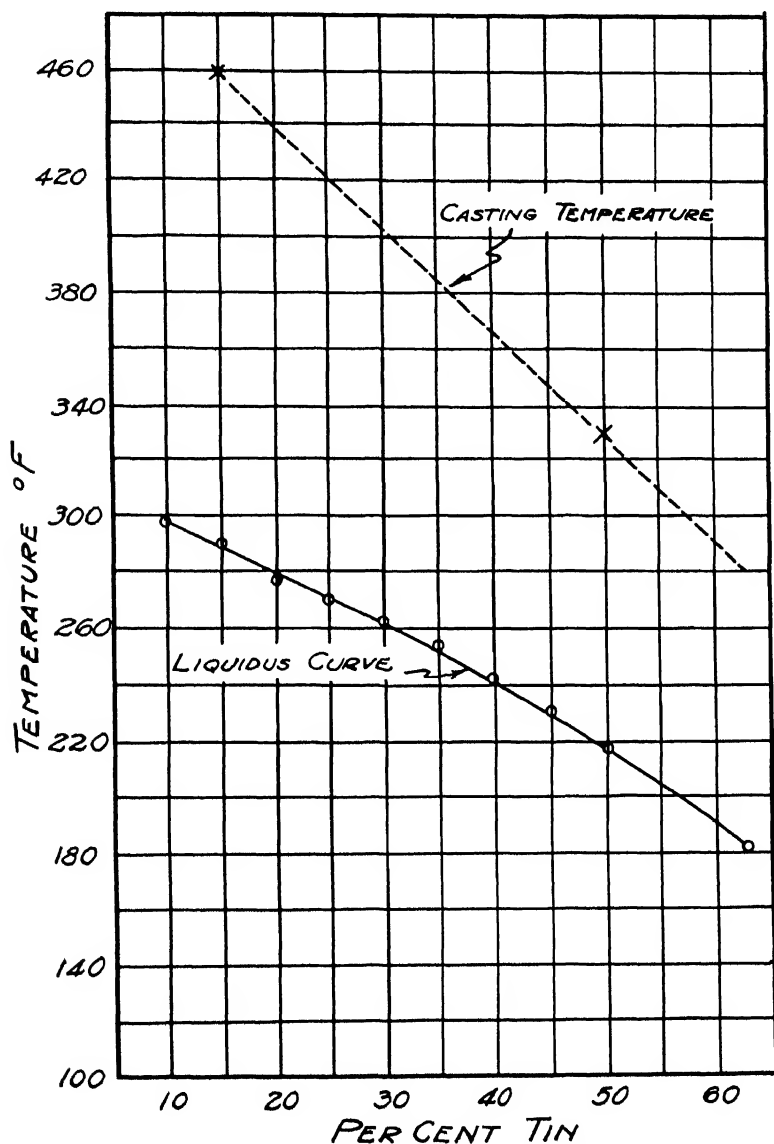


FIG. 2.—RANGE OF TEMPERATURES USED IN CASTING CONDUCTIVITY SPECIMENS.

From preliminary tests made on the effect of casting temperature on castability, it was determined that solders near the eutectic in composition had much better casting properties than those of high lead content. An effort was consequently made to compensate for this by using a greater

superheating range on the high-lead solders than on those nearer the eutectic composition.

Casting temperatures for the conductivity tests were chosen as shown in Fig. 2. The liquidus curve is taken from Stockdale³. Temperatures found most suitable for the various molds and for casting test specimens other than those for conductivity tests were as follows:

Mold	Casting Temperature, Deg. C., Above Liquidus	Mold Temperature, Deg. C.
Conductivity.	(See Fig. 2)	75
Impact	100	60
Shear	60	75
Tensile.	65	155

Electrical Conductivity.—Specimens for electrical conductivity tests were cast in an open split mold made of rolled steel, $\frac{3}{4}$ by 1 by $19\frac{1}{2}$ in., over all. Thermocouples, set in small holes at both ends and at the center of the mold, came within $\frac{1}{16}$ in. of the casting wall. The cast specimens, $\frac{1}{4}$ by $\frac{3}{10}$ by $18\frac{1}{2}$ in., were machined sufficiently to produce a square cross section, accurately measured by micrometer at inch intervals, and tested for conductivity 24 hr., after casting by means of a Kelvin bridge maintained at 30° C. by an automatically stirred oil bath. Three specimens were tested for each alloy and the average was taken as the conductivity. Variation between specimens of the same alloy amounted to much less than 0.1 per cent of the conductivity of copper.

Results of these tests are given in Table 2, as calculated to the percentages of the conductivity of copper. The greatest variation between the four different solders is only 0.2 per cent of the conductivity of copper, hence for all practical purposes they may be considered to have equal conductivity.

Series C alloy, made from electrolytic solder adjusted with Straits tin, has a consistently higher conductivity through the most used solder range, 25 to 45 per cent tin. All the variations are explainable by comparing the impurities present. In the lower-tin solders the secondary metal gives the lowest conductivity; in the high-tin range the influence of impurities in the Chinese tin added to electrolytic solder becomes noticeable.

In order to compare the effect of aging on the electrical conductivity of solder, one bar from each alloy was retested after remaining at room temperature for from six to eight months. This comparison is given in Fig. 3, where a very exaggerated scale is used to disclose any small differences that may be present due to differences in composition of the four classes of solder. An increase in conductivity of about 5 per cent occurred by

TABLE 2.—Physical Properties of Lead-tin Solders

Sn, Per Cent	Conductivity, Per Cent of Cu Std. at 30° C.				Charpy Impact, Ft.-lb.				Shear, Lb. per Sq. In.				Tensile Strength, Lb. per Sq. In.				Elongation, Per Cent in 2 In.			
	Alloy Series				Alloy Series				Alloy Series				Alloy Series				Alloy Series			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
15	8.40	8.38	8.36		8.7	12.2	12.5		4,470	4,690	4,500		5,680	5,590	5,610		18.0	16.5	17.3	
20	8.73	8.63	8.61	8.68	12.2	18.9	12.4	14.2	4,740	4,370	4,690	4,970	5,800	5,730	5,320	5,630	16.0	18.0	12.0	18.0
25	8.98	8.88	9.04	8.95	13.4	18.9	11.7	10.8	5,310	5,260	4,850	5,180	5,990	5,830	5,700	5,890	27.0	21.0	21.0	21.0
30	9.25	9.23	9.37	9.32	17.7	17.5	15.7	13.1	5,500	5,430	5,240	5,640	5,990	5,890	5,780	6,110	31.0	35.0	30.0	31.7
35	9.59	9.54	9.79	9.57	18.6	17.7	19.5	17.1	5,590	5,610		5,890	6,280	6,210	6,050	6,500	26.0	40.0	35.0	40.0
40	10.08	9.98	10.16	9.99	19.0	17.4	19.7	15.0	5,680	5,750	5,680	6,090	6,250	6,320	6,080	6,480	49.0	45.0	50.0	39.5
50	10.91	10.78	10.90	10.74	15.9	16.1	16.7	16.3	5,870	5,870	5,770	6,320	6,090	6,130	5,950	6,360	74.0	72.3	61.9	60.5
63	11.82	11.79	11.76	11.70	14.2	14.5	13.0	13.9	6,060	5,920	5,890	6,230	7,490	7,570	7,060	7,680	29.5	27.5	33.7	38.8

aging throughout the alloy range for all the solders. Tests on series A solder, 40 per cent tin, gave a 0.7 per cent increase in conductivity by aging at room temperature for 48 hr. in place of the usual 24-hr. period;

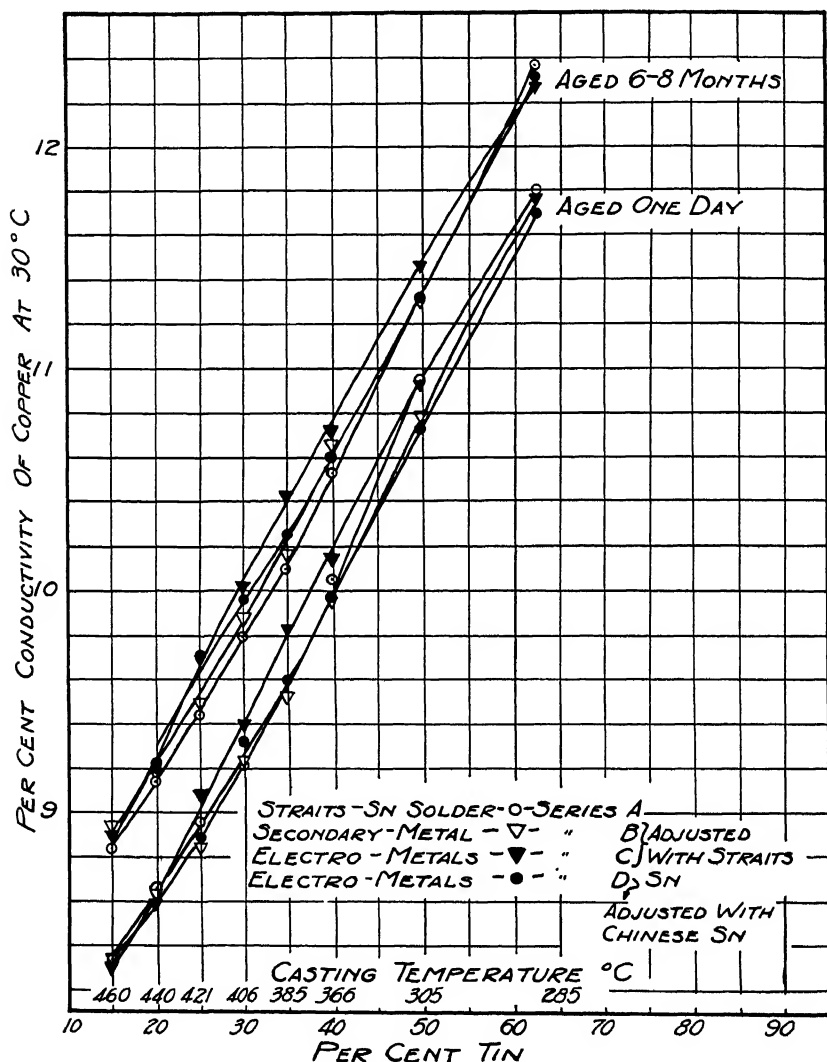


FIG. 3.—EFFECT OF AGING ON THE ELECTRICAL CONDUCTIVITY OF LEAD-TIN SOLDERS.

by annealing for 16 hr. at 100° C. during the second 24-hr. period a conductivity increase of 2 per cent was secured.

Impact Strength.—Five standard, notched Charpy impact specimens were cast in one bar by using a split mold made of rolled steel, 3 by 2 $\frac{3}{8}$ by 13 in. in size, equipped with a 1 $\frac{1}{2}$ -in. riser and sprue of the same height.

As shown in Fig. 1, the notches were cast in place. Mold temperature control was obtained by means of the usual thermocouple arrangement at the center and ends of the bar. Individual specimens were sawed from the bar and tested on an Amsler impact machine approximately 24 hr. after casting. Two and sometimes four bars were tested, making a total of 10 to 20 tests for each alloy.

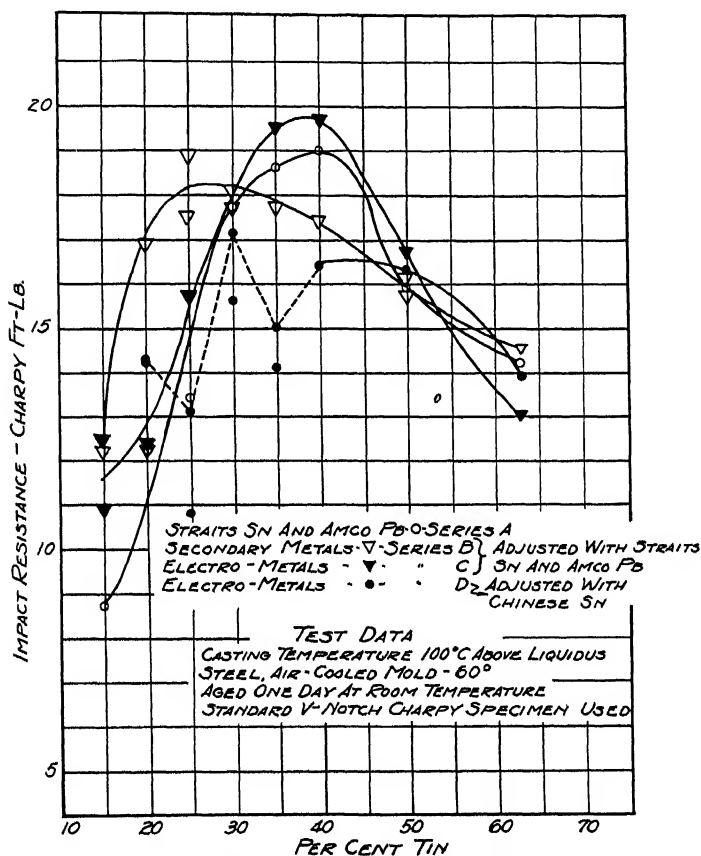


FIG. 4.—CHARPY IMPACT RESISTANCE OF SERIES A, B, C AND D SOLDERS.

Results of the average values obtained are given in Table 2. In Fig. 4 the average impact values are plotted on a greatly exaggerated scale to show any particular influence given by differences in composition of the solders. From the nature of the test it is difficult to secure close checks on individual specimens; however, treating the average from a five-specimen bar as a unit, impact values usually varied less than one foot-pound and for the high-tin solders the agreement of individual tests was still better.

In interpreting these results only general trends should be considered. The erratic values for series D solder, which were checked, are probably due to the variations in copper and iron impurities added with the Chinese tin. Possibly the relatively high silver content of the series B solder accounts for its difference in behavior, or its low iron content in the lead-rich solders may have an influence on the impact strength. For

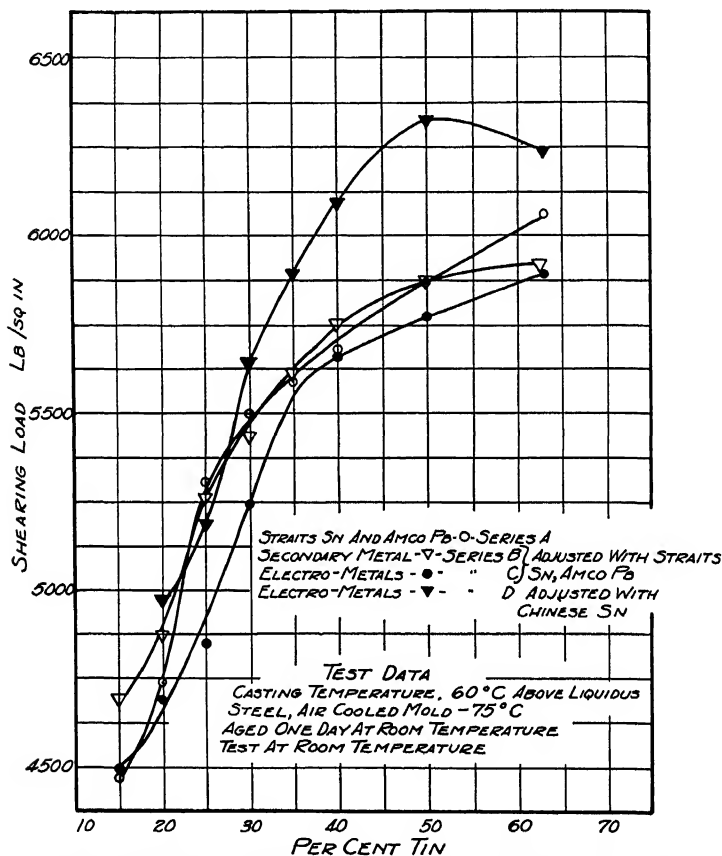


FIG. 5.—SHEARING STRENGTH OF SERIES A, B, C AND D SOLDERS.

the purest solders it is very evident that maximum impact strength is secured with a composition of 35 to 40 per cent tin.

To completely determine the effect of various impurities on the impact strength, many more tests are needed on a pure solder to which single impurities are added.

Shearing Strength.—The mold used for casting shear-test specimens, as illustrated in Fig. 1, was a massive, 3¾ by 6-in. dia., split, cold-rolled steel mold, fitted with a cover that acts both as a core to form the inside

ring section and as a riser. This gave a casting similar to a plug soldered into the end of a close-fitting ring. It is a type advocated by Nightingale⁴.

In making the tests, the ring portion (3 in. outer dia., 2 in. inside dia.) was suitably supported in a 72,000-lb. hydraulic Amsler tensile machine and the plug portion was forced out under compression by a $1\frac{1}{4}$ -in. mandrel. This gave a circular shear of $\frac{1}{4}$ in. over a diameter of about 2 in., or over an area of 1.56 sq. in.

Three to six specimens were tested on each solder at a constant loading rate of 4000 lb. per min. Tests were made about 24 hr. after casting. Maximum variation in data obtained was 200 lb. per sq. in. Tests on many solders in the high-tin range gave results with a variation of less than 75 lb. per sq. in., or a spread of less than 1 per cent.

Average results of the shear tests are given in Table 2 and Fig. 5. The shear strength of the secondary and the virgin metal solders were nearly the same throughout most of the composition range. As would be expected, the purer electrolytic solder adjusted with Straits tin, series C, was consistently lower in shear strength and appeared to fracture more gradually. The electrolytic solder containing appreciable amounts of copper, bismuth and iron, because of the addition of Chinese tin, series D, gave a much higher shear strength in the higher-tin compositions and was noticeably stiffer, since it tended to break with a snap. It is probable that the difference in behavior of series D solder is due to its copper content, as the highest strength solder (50 per cent tin) coincides with the highest percentage of copper.

To indicate the effect of varying the rate of loading on shear strength, some series C solder specimens were sheared at the rate of 20,000 lb. per min. These gave the following results:

SHEARING STRENGTH, LB. PER SQ. IN.

Sample	Rate of Loading, Lib. per Min.	
	4,000	20,000
C 35	5,600	5,910
C 63	5,900	6,830

Tensile Strength.—Tensile bars were cast horizontally in a split, cold-rolled, mild-steel mold equipped with a 2-in. graphite sprue. The mold was made $1\frac{1}{2}$ in. square by $8\frac{3}{4}$ in. to give a specimen $7\frac{5}{16}$ in. long with a 2-in. parallel central section having a diameter of $\frac{3}{8}$ in. Shoulders $\frac{5}{8}$ in. square and $1\frac{1}{2}$ in. long were used.

Considerable difficulty was experienced in getting sound castings in tensile bars, and it was only after trying various kinds of molds, graphite as well as steel, various dimensions for the specimen and risers, and many changes in procedure that consistent results were secured.

Care was necessary in removing the specimens. By partially cooling in the mold, danger from hot-short cracks was eliminated. A relatively high mold temperature, 155°C ., was used to secure the desired castability. This necessitated slight cold-working of the shoulders of the high-lead specimens, to prevent breakage at or near the shoulders during testing.

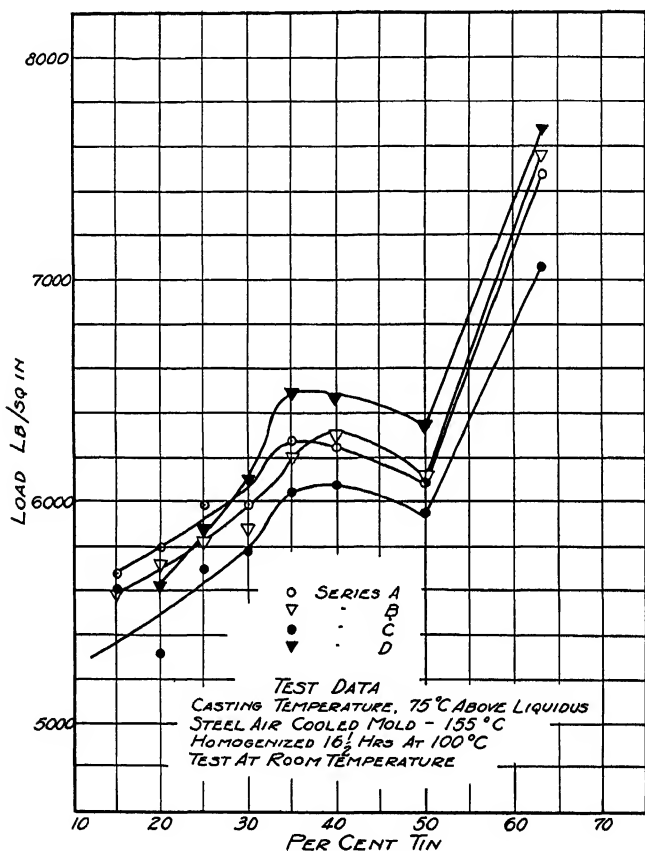


FIG. 6.—TENSILE STRENGTH OF SERIES A, B, C AND D SOLDERS.

Tensile bars were all annealed for 16 hr. at 100°C . in a water-jacketed muffle before testing. This was largely to relieve any strains that might be established in removing the bars from the mold and to effect stabilization.

Specimens were tested on a 1000-lb. Amsler testing machine at a constant rate of travel of the free cross head of 0.5 in. per minute. During the time that stress is proportioned to strain, this gave a strain rate of about 0.1 in. per minute, since the weighted arm permits a downward movement of the upper jaw.

Results of the tensile tests, an average of three tests on each solder of a given composition, are given in Table 2 and Fig. 6. The strengths at any given tin-lead composition of each of the four classes of solder do not differ by as much as 10 per cent. As in the shear tests, the purest solder, series C, consistently gave the lowest strength throughout. Likewise, the series D electrolytic solder, containing impurities from the Chinese tin added to bring the tin content above about 25 per cent, gave consistently the highest strength. This may be attributed largely to the

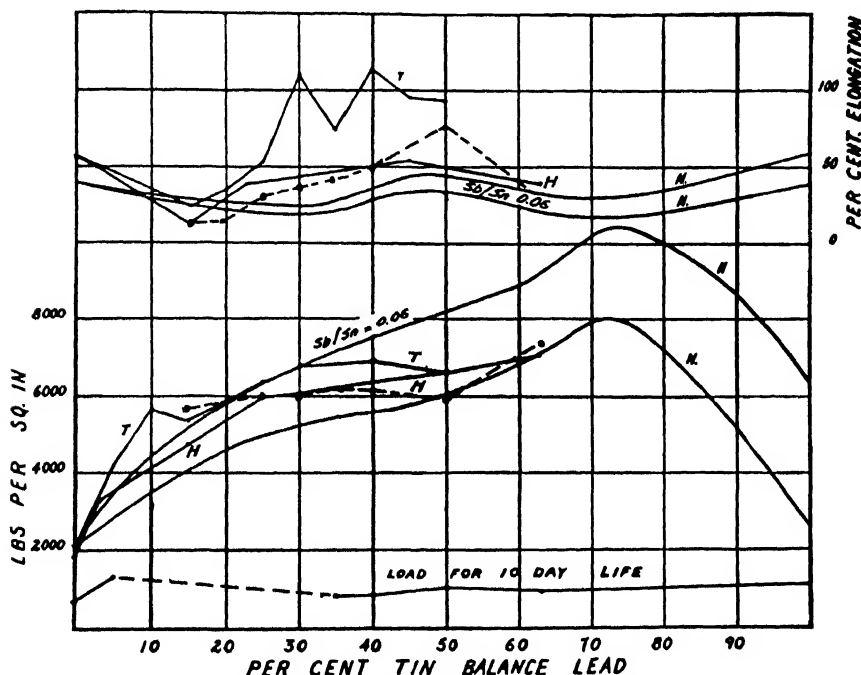


FIG. 7.—RESULTS OF TENSILE-STRENGTH TESTS BY OTHER INVESTIGATORS. AUTHORS' RESULTS ARE SHOWN BY DOTTED LINE.

copper in the higher tin compositions of this solder. As in the shear tests, the secondary solder and virgin metal solder gave almost identical values. Variation in results between the three samples tested for each solder did not exceed 2 per cent, and usually varied much less than that.

Values for unannealed tensile specimens would be much higher than those secured in these tests. A faster rate of testing would also greatly raise the tensile-strength results. As cast, the A-63 alloy (63 per cent Sn) was over 20 per cent stronger than after annealing, and the A-40 alloy over 16 per cent stronger before annealing.

Values for 40 and 50 per cent tin solders are low, for two reasons—a decidedly slower freezing rate and a greatly increased rate of elongation. Neither of these conditions is present to any extent with the shear or

the soldered-joint specimens, especially not with the latter. However, this break in the curve is not of great importance, as it is the comparison between different types of solders of the tin content that is concerned here. In Fig. 7, the authors have superimposed values of series A, represented by the dashed line, on a graph comparing tensile data on somewhat similar material by Nightingale, Thompson and G. O. Hiers⁵. The

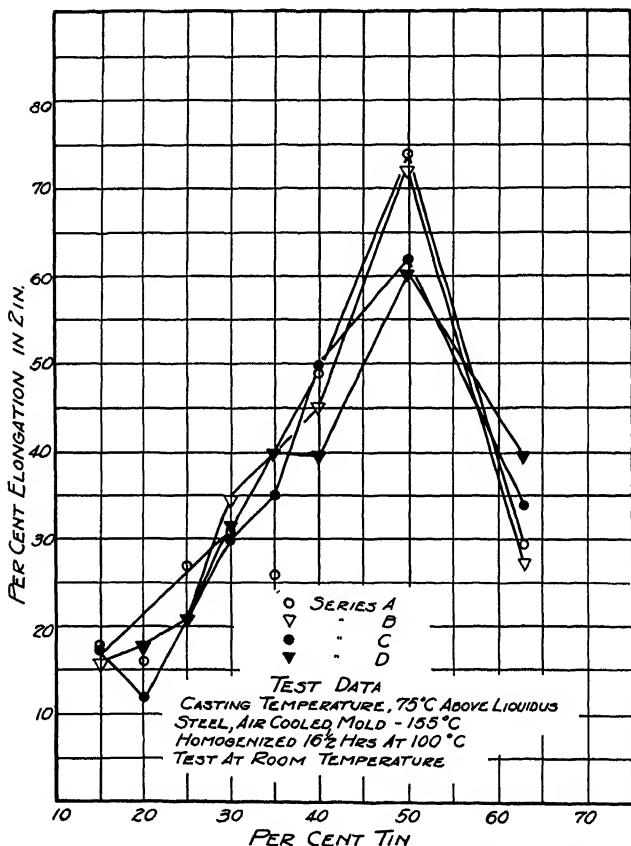


FIG. 8.—ELONGATION OF SERIES A, B, C AND D SOLDERS.

curves of Thompson and Nightingale give or tend to give the same dip at 50 per cent tin. The comparatively high values of lead-rich alloys shown by the dotted line are due to a greater antimony-tin ratio than was used by the other investigators.

Elongation.—The average elongations of the tensile specimens are recorded in Table 2 and shown graphically in Fig. 8. Although somewhat erratic, the general trend from low values in the lead-rich solders to a maximum in the 50-50 region is marked.

Irregularities in elongation may be due to very slight difference in the internal structure of the specimen, as well as to possible slight variations in casting technique, such as uniformity of soot on the molds. As a comparison, Thompson⁶ reports the following elongations on solders, as cast:

Tin, Per Cent	Elongation, Per Cent in 2 In.	Tin, Per Cent	Elongation, Per Cent in 2 In.
25	54	40	117
30	109	45	97
35	75	50	96

Elongations of up to 150 per cent have been secured on some of the 50 per cent tin solders that were cast into a mold at 60° C. and pulled with a free cross-head travel of 0.1 in. per minute instead of the usual rate of 0.5 in. per minute. The 50 per cent tin solders, either as cast or annealed, showed decidedly greater elongation than any of the solders from 15 to 63 per cent tin that were subjected to similar treatment. From a limited number of tests, elongations were found to be about the same whether annealed or not.

SOLDERED-JOINT TESTS

In attempting to determine differences in strengths of soldered joints due to comparatively minute differences in solder composition, it was decided, after preliminary tests, to use a comparatively simple, inexpensive type of joint such as a single lap joint. A more elaborate joint, such as the "plug and ring" test used by Nightingale⁴, undoubtedly does give a true shear value but a lap joint gives a combination shear-tensile loading such as is met in most types of service.

Joint members were made from half-hard, cold-drawn 70-30 brass. Each member was made 4 in. long with a $\frac{1}{8}$ by $\frac{3}{8}$ -in. cross section. The members overlap to give a $\frac{7}{16}$ -in. soldered section, as shown in Fig. 9. Solders used in these joint tests were the same as those used in making physical tests. All joints were fluxed with an aqueous solution of zinc chloride and ammonium chloride in approximately the eutectic ratio of these salts; i.e., a 5:2 ratio.

Soldering Apparatus and Procedure.—Fig. 9 shows a sketch of the jig used in holding the joints while they were being soldered. Heat was applied by means of a gas burner, the temperature being measured by a small thermocouple inserted through a small hole drilled into the side of one joint member. Clamps were placed 2 in. apart.

Two methods of soldering the joints have been used. In the first or "closed method," the properly prepared members, rigidly fixed in the jig at a definite joint clearance of 0.007 in., were soldered in place in the normal way and no change was made until the solder solidified. In the

second or "open method," which gave a much better joint, the same preliminary procedure was followed, but instead of holding the joint open to only 0.007 in. during the actual soldering operation it was opened to about 0.030 in. After the solder was applied the joint was squeezed back to the normal 0.007-in. opening while the same soldering temperature was maintained.

By either method, the brass strips being prepared for soldering were cleaned in carbon tetrachloride, pickled in chromic acid almost to the point of etching, and rinsed, then flux was brushed upon the surfaces to

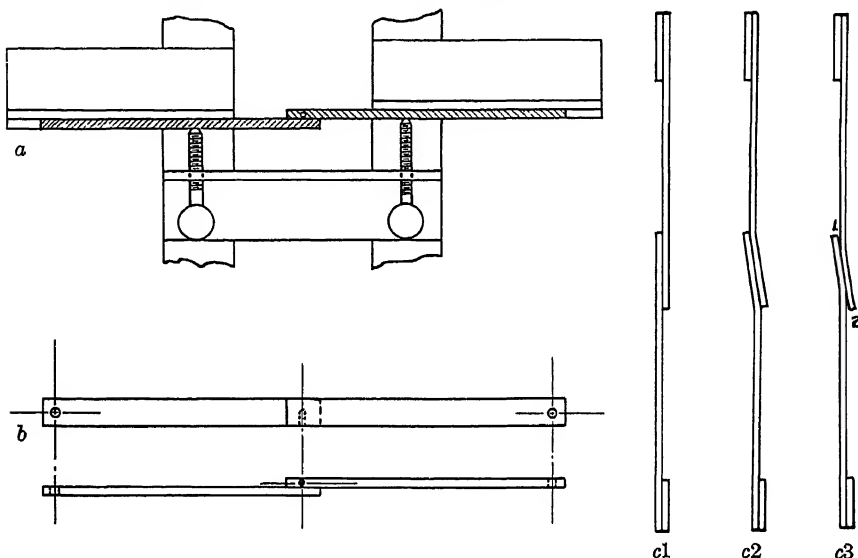


FIG. 9.—APPARATUS FOR MAKING AND TESTING SOLDERED LAP JOINTS.

a, jig-top view; *b*, brass lap joint; *c*, thin lap joint in tension.

This assures exact duplication of soldered areas. The jig is adjustable to give definite control of the overlapping and clearance of the joints.

be soldered. After heating in a free flame these surfaces were tinned with the solder to be used, the excess shaken off and the strips cooled. Subsequent brushing with dilute flux removed excess flux and left a definite amount preparatory to soldering. Specimens were then placed in the jig, heated to 75°C . above the liquidus temperature of the solder to be used and stick solder applied. The temperature was brought up quickly, and if lowered during the application of solder the gas flame was retained only until the proper heat was attained. Joint members were unclamped at one end just as the solder set, in order not to introduce any strains while cooling. Before testing, all excess solder was filed away so that only the solder in the joint itself had any effect on the joint strength.

Method of Testing.—Testing of finished joints was done on a 1000-lb. Amsler tensile machine. These lap joints were pulled in the same manner

and at the same speed as the tensile-test bars; that is, with a movable jaw speed of 0.5 in. per minute. The jaws of the machine came within an inch of the joint proper and were self-aligning. By inserting at the extremities of the joint pieces of brass of the same thickness as the joint sections, as shown in Fig. 9c-1, some compensation was made for the offset character of the joint.

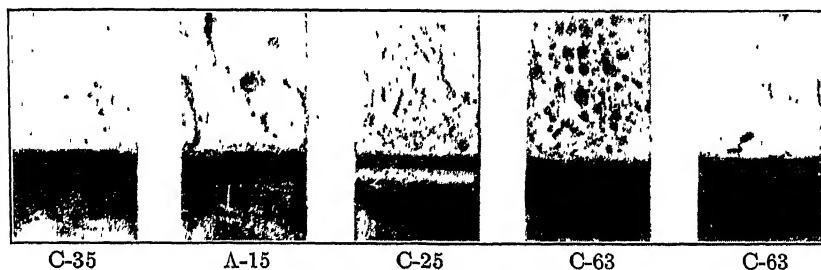


FIG. 10.—BRASS LAP JOINTS BY CLOSED METHOD OF SOLDERING, SHOWING POROSITY AND FLUX INCLUSIONS.

Joints were made by the closed method on each solder until sufficient solid joints were produced to give a fair comparison. Only a few were required on the 35 and 40 per cent tin solders because they were comparatively free from porosity; 12 or 13 tests were necessary in order to secure a few sound joints with some compositions. Soundness of joints was determined by inspection without regard to the strength secured on testing. Fractures of typical joints made by the closed method of soldering, showing different degrees of porosity, are illustrated in Fig. 10.

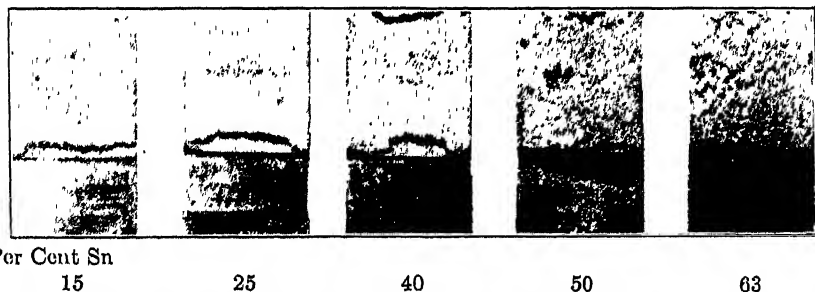


FIG. 11.—REPRESENTATIVE BRASS LAP-JOINT FRACTURES BY OPEN METHOD OF SOLDERING, SERIES A.

By using the "open method" of soldering, porosity was practically eliminated from all joints regardless of the composition. The wider opening between the joint members when applying solder permits a washing action that insures a thoroughly wetted surface, whereas the very thin opening used in the closed method encourages the trapping of flux and air. Typical fractured joints made by the open method are shown in Fig. 11.

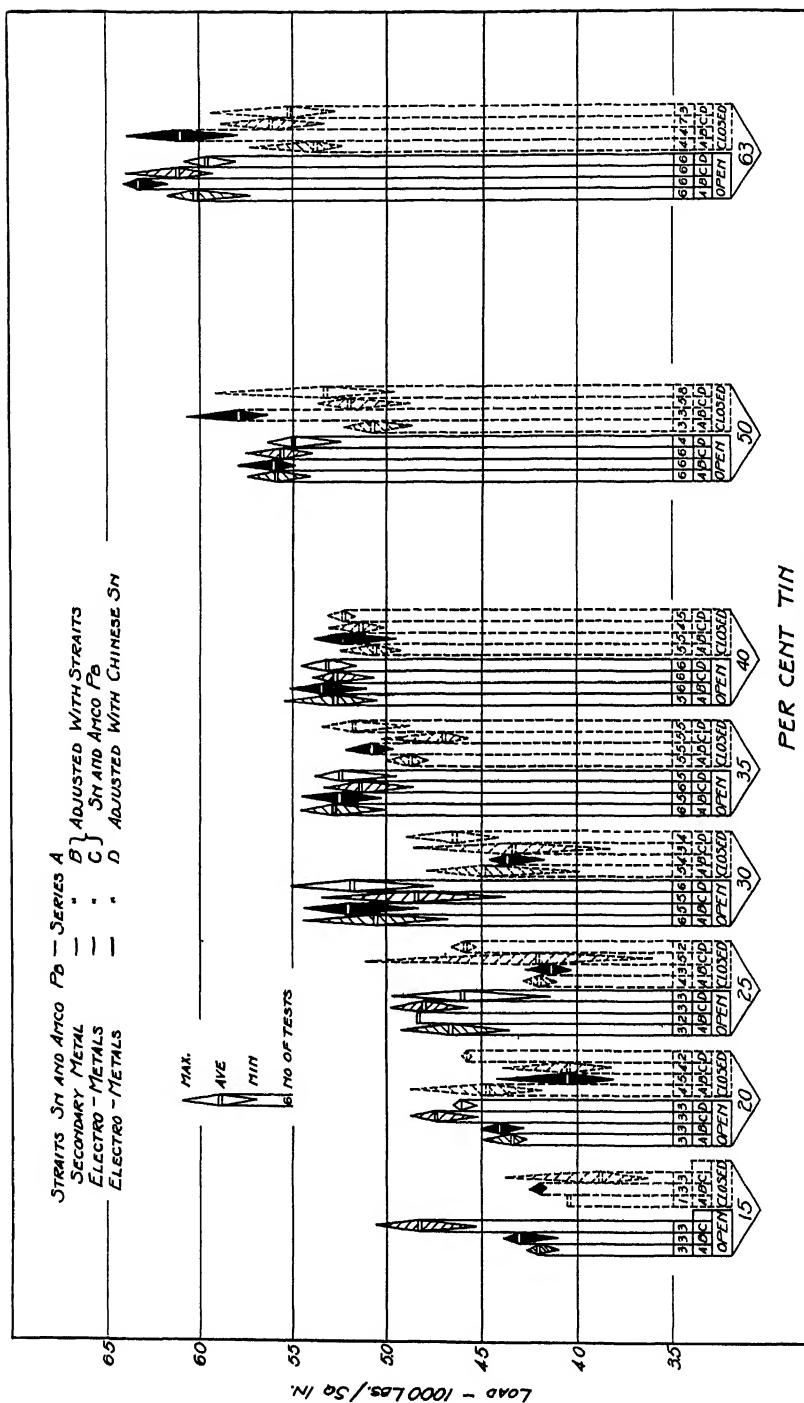


FIG. 12.—RESULTS OF TESTS ON LAP JOINTS.

Three joints were made from each composition of each of the four different classes of solder under investigation. Later two or three more joints were made to duplicate the results obtained on the more important compositions of from 30 to 63 per cent tin. In order to make direct comparisons between results obtained from these four series of solders, the same strip brass and soldering conditions were used for each group of joints. All joints were tested one day after they were made.

Results of Joint Tests.—The strengths of soldered joints, as obtained by the closed method of soldering, are given in Table 3; those obtained by the open method are listed in Table 4. All results are listed, not just to record the variance in results but to show the differences in soundness of joints obtained.

Fig. 12 is a graphical representation of the strengths of *sound* joints. For purposes of comparison, results obtained by the two methods of testing have been grouped together, as well as results of the four series of solders being investigated.

DISCUSSION OF RESULTS

The open method of making joints was so effective in eliminating unsoundness that results with this method are much to be preferred over those of the fixed closed joint. The latter proved advantageous in a qualitative way, however, for determining solders that gave the best fluidity and were least affected by any tendency to form porous spots and flux inclusions when solder is run into narrow joints. Higher average values were obtained by the open method and, in general, less scatter of results.

As a comparison with another type of joint, some results obtained by Nightingale⁴ on nonantimonial solders used in a 60-40 brass "ring and plug" shear test gave the following values:

SHEAR STRENGTH, LB. PER SQ. IN.			
Percentage of Tin			
65	55	45	33
2260	5750	4050	5500
2220	3425	5110	3995
2555	4590	4340	3905
		6270	4770
		5510	
		4700	

These results were secured by a closed method of soldering using a plug clearance of 0.003 in. Even with this rather elaborate method of

testing, considerable scatter in results was obtained; indeed, much more than we have encountered in using a single lap joint.

TABLE 3.—*Strength of Soldered Lap Joints, Closed Method*
POUNDS PER SQUARE INCH

Tin Content, Per Cent	Series				Tin Content, Per Cent	Series			
	A	B	C	D		A	B	C	D
63	5250	5950*	5210*	5960	50	4520*	6090	5140	5100
	4640*	6400	4780*	5270*		5140	5950	5380	4980
	5300*	6290	5470	5550*		5240	5510*	4980*	4970
	5290	5800	5610	5280		4870	5650	5240	4410*
	5260	5950	5550	5330		5050*	5540*	5120*	5120*
	4980*	5940*	4980*	5280*				4870	5490
	5040*		5410	6240*				5090*	5380
	5750		5900	5630*				5360	5560*
			5740	4980*					5330
			5615						5260*
									5940
									5500
40	5050	5330	5300	5250	35	4860	4960	4710	4860
	5250	4940	5200	5220		4890	5100	4660	5275
	5040	5160	5030	5300		4780	5220	4560	5100
	5070	5340	5000	5170		4820	5020	4930	5340
	4910	5380	4770*	5160		5000	5090	4620	5250
30	3980	4410	3900*	2800*	25	440*	4020	2220*	4225*
	2290*	4460	4290	4260*		2670*	4100	1400*	3420*
	4600	4420	3820	4410		3060*	3590*	3280*	4600
	4560	4430*	2220*	4440*		2580*	4280	3020*	4525
	2820*	4170	2790*	4410		4300		3000	3790*
	4500		2340*	4415*		4120		4100	
	4260*		4130*	3240*		4100		4550	
	4790		3740*	4840		4300		3890	
	4510*		2650*	4460*				5120	
	4430*		4020*	4070*					
			3320*	4130*					
			3480*	3270*					
			4860	4900					
20	4010*	3800*	4390	4560	15	3720*	3810*	3640	
	4550	4440	3810	4660*		4120*	4260	4380	
	4290	4000*	4000	4175*		3280*	3360*	3620	
	3725*	3880	3990	4070*		3160*	4160	3560	
	4880	4615*		4600		3840*	4160		
	4020*	3810		3800*		4075*			
	3790*	4070		3670*		4050			
	4180	4040		3640*		4090*			
						4050*			
						2990*			

* Values omitted because of porosity or excessive flux inclusions.

Series B solder, made from secondary metal, was qualitatively the best of the four classes of solder for producing good joints. This is indicated in Table 3, where fewer joints were discarded because of porosity than with the other series; and also in Fig. 12 and Table 4, where less

scattered results were secured than with the other solders. The high silver content of the series B solder may be at least partly responsible for this behavior.

Solders of series A and C were improved most by changing to the open method of making the soldered joints. Values were raised and less

TABLE 4.—*Strength of Soldered Brass Lap Joints, Open Method*
VALUES, POUNDS PER SQUARE INCH

Tin Content, Per Cent	Series				Tin Content, Per Cent	Series			
	A	B	C	D		A	B	C	D
63	6150	6400	5930	6440	50	5515	5550	5410	4970 ^a
	6020	6380	6100	5900		5550	5610	5519	5250
	5740	6175	6000	6090		5410	5490	5470	5460
	6090	6350	6400	5810		5700	5800	5710	5650
	5940	6380	6180	5990		5750	5820	5610	5070 ^a
	6170	6310	6110	5990		5700	5750	5770	4700 ^a 5620
40	5160	5260	5200	5150	35	5100	5160	4850	4950
	5200	5360	5200	5330		5410	5025	5050	5025
	5040	5100	5050	5150		5350	5350	5110	5225
	5550	5340	5330	5450		5330	5200	5190	5330
	5400	5490	5400	5370		5460	5440	5330	5380
		5515	5400	5410		5010		5290	
30	4900	4820	4670	5220	25	4700	4830	4860	4915
	4510	4880	4635	4750		4930	4830	4570	4750
	4675	5440	4370	4780		4350		4975	4140
	5385	5400	5350	5400					
	5450	5450	5160	5510					
	5450			5385					
20	4280	4510	4880	4520	15	4250	4435	4930	
	4265	4425	4850	4660		4265	4390	5050	
	4490	4280	4520	4660		4100	4100	4520	

^a Values omitted because of porosity or excessive flux inclusions.

scatter in results secured. Considering the four solders as a whole, however, the strengths of soldered lap joints secured were very similar for any given composition. The strength increased with fair uniformity as the tin content was increased, within the limits of the compositions studied. R. Rolleston West⁷, after experimenting with solders for tin cans, also reported that a 35 per cent tin solder gave the most solid and reliable joint. He also found that the eutectic solder (63 per cent tin) produced a porous joint.

In tinning brass joints with eutectic solder, no trouble was experienced until after the brass was tinned, then an excess of solder would refuse to

wet the newly tinned surface. This phenomenon was also noted at times with 50-50 solder. Porosity in the high-lead solders appeared to be due to other factors, especially reduced flowability.

GENERAL CONCLUSIONS

In this investigation some of the fundamental properties of four classes of solder have been compared in massive form by means of electrical conductivity, impact, shear and tensile tests, and as thin films in soldered brass lap joints. No great differences in behavior are shown by these solders but the following specific conclusions may be drawn.

1. The purest solder, electrodeposited and adjusted with Straits tin, gives a slightly higher electrical conductivity through the most used composition range, but the differences in conductivity between the solders tested is too small to be of any practical importance.

2. There is approximately a 5 per cent increase in the electrical conductivity of all the solders upon aging at room temperature for six or eight months.

3. There is no difference of practical import as to the tensile and shear strengths among the four classes of solder tested, but the more impure solders, as the high-tin solders of series D, are slightly stronger, and the purest electrolytic, or series C, solder is somewhat less strong, than the average.

4. The impact strengths of the solders made from virgin metals and electrolytic solder adjusted with Straits tin are nearly the same, and reach a maximum with a tin content of about 40 per cent. Secondary solder containing silver and very small amounts of other impurities has a much higher impact value than the other solders in the high-lead range. The addition of copper to electrolytic solder appears to definitely injure its impact strength.

5. In good, solid joints there is little practical difference among the four classes of solder tested; however, fire-refined secondary solder gave slightly stronger joints than the other solders, and more consistent results with less difficulty due to porosity.

6. All types of solders containing 35 and 40 per cent tin that were tested produced markedly superior joints when soldered by either closed or open method.

7. A method of soldering joints has been devised that practically eliminates porosity and gives satisfactorily comparable results using single lap joints. This consists essentially of flowing solder into a properly prepared wide joint, then forcing the joint members to the desired standard narrow width while the solder is molten.

8. From this general information on the behavior of several classes of solder over a wide lead-tin composition range and with the methods

of testing bulk solder and joints that have been developed, a foundation has been laid for further work, of practical aim, on the effect of single impurities and of various factors affecting the behavior of these solders.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to the United States Metals Refining Co., Carteret, N. J., for furnishing the solder used in these investigations, and to the spectroscopist of that company, Mr. R. G. Ernst, for so ably analyzing all the various solder compositions used. To Dr. O. E. Harder, of Battelle Memorial Institute, and Mr. D. L. Ogden, of the United States Metals Refining Co., many thanks are due for their counsel and suggestions at all times during this investigation.

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DISCUSSION

(J. G. Thompson presiding)

G. E. DOAN,* Bethlehem, Pa.—May it not be, as it appears from the paper, that the properties of the *liquid* solder are more important in determining the success of the soldering operation than the properties of *solidified* cast bars such as the authors used in their experiments? For example, the solubility of gases in the liquid solder and the rate of escape of those gases might be the determining factors in deciding which solder is superior. So it seems to me, in order to obtain a complete story of the effect of composition on solder properties, some attention should be given to the properties of the liquid solder also.

B. W. GONSER.—That is largely included in the term "fluidity," is it not? Several different factors enter and we should like to have continued, and have continued to some extent, a comparison of properties of the various solders in the liquid state. We notice differences in fluidity in the different solder compositions. Mr. Heath will mention some of the differences found in the behavior of liquid solder.

C. M. HEATH—Comparison of results obtained by the open and closed methods of soldering brings out the importance of such characteristics as fluidity. Joints

* Associate Professor of Metallurgy, Lehigh University.

made by the open method were much less porous, showing that the movement of the liquid metal and the squeezing action permitted escape of entrapped gases, thereby producing a better joint. Considerable information on comparative fluidity is given by comparing the porosity of joints secured by the closed method (Table 3). The number of tests discarded because of porosity indicate the compositions that gave the most sluggish liquid solder. A solder containing 35 or 40 per cent of tin produced good joints by both methods of soldering.

J. G. THOMPSON,* Washington, D. C.—My own experience in testing solders or such soft metals has been rather limited, but has demonstrated that it is unusually difficult to get reproducible consistent results. I think the authors are to be congratulated in that respect, at least.

H. R. FRECHE,† New Kensington, Pa.—In testing the lap joints, did you find that the failure occurred in the soldered metal or along the interface? Did you make any microscopic examination of the joints to determine the extent and character of diffusion?

C. M. HEATH.—The fracture took place in the soldered metal but usually near the interface; that is, some solder would adhere to both members of the joint but most of it adhered to one member. (See Fig. 11.)

We were not particularly concerned with diffusion, rather with seeing what differences there would be in properties of the different types of solder when using the same experimental procedure. We did not have time to make metallographic examinations of the joints.

C. E. SWARTZ,‡ Cleveland, Ohio.—Inasmuch as the authors used a constant distance between the two halves of the specimen, they were able to get a more uniform breaking strength than ordinarily is obtained in the hand soldering operation, and in the machine soldering operation as well. The strength of the joint varies markedly with this difference in distance between the two halves of the soldered joint. If this distance is too great, there occurs what might be called, in ordinary language, plastic flow of the pure solder at the center of the solder joint. If the distance between the two halves is too small—that is, too much pressure has been applied after the solder was run into the joint—the result is largely an intermetallic compound, which is rather brittle, and the joint will be somewhat more brittle than if the distance is medium; say, 0.007 in., as the authors used. I do not know just how they arrived at the 0.007, but I should think that would give an intermetallic layer on both sides of essentially plastic solder at the center of the joint.

B. W. GONSER AND C. M. HEATH (written discussion).—We heartily agree with Dr. Doan that properties of the liquid solder are important. Factors described by the overlapping terms of surface tension, fluidity, penetrability and wettability, as well as surface preparation by use of fluxes, greatly influence the behavior of solder. Our comparison of properties of solidified cast bars was a step in observing the effect of differences in composition or methods of manufacture on physical properties, to be supplemented by actually making joint tests that involve many properties.

There is no particular reason to believe that gases are absorbed by the liquid solder and released on solidification. The porous joints we secured were due to occluded air or bubbles, since by squeezing a wide joint while the solder was still liquid a solid joint resulted.

* National Bureau of Standards.

† Aluminum Research Laboratory.

‡ Cleveland Graphite Bronze Co.

A distance between joint members of 0.007 in. was arbitrarily taken because it was a standard not difficult to duplicate. We found practically no difference in the strength of solder layers varying in thickness from 0.003 to 0.007 in. The latter was taken as standard because it was easier to get nonporous joints with a thicker solder layer using the closed method. Later, the same distance was kept in the open method of soldering merely for comparison with previous results. A distance of less than 0.003 in. was unsatisfactory for the reasons stated by Dr. Swartz; a distance of over 0.007 in. seemed impractical.

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